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Source Test and Evaluation Report Cane Run Unit No. 6, Louisville Gas and Electric Company

TRW Environmental Engineering Div.
Redondo Beach, CA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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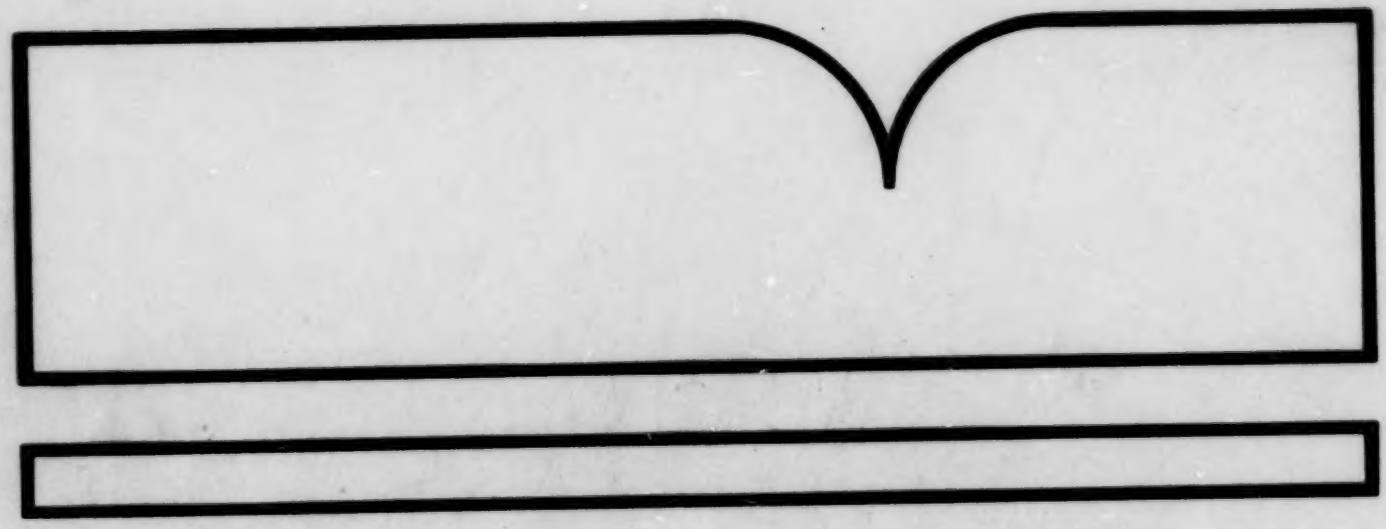

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SOURCE TEST AND EVALUATION REPORT: CANE RUN UNIT NO. 6, LOUISVILLE GAS AND ELECTRIC CO.

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16. ABSTRACT The report gives results of a comprehensive multimedia emissions assessment of a coal-fired boiler equipped with electrostatic precipitators (ESPs) and a dual-alkali flue gas desulfurization system. Flue gas pollutant concentrations were measured at the inlet and outlet of both control devices. Scrubbing efficiency for SO2 was 88%. Particulate removal efficiencies were 99.7% across the ESPs and 19% across the scrubbers for a total removal efficiency of 99.86%. Particulates (exclusive of H2SO4 aerosol) less than 3 micrometers in diameter accounted for 59% by weight of total particulate emissions. Emissions of primary sulfates averaged 6.6 ng/J, or 2% of total sulfur species emitted. Primary sulfate removal efficiencies were 48% across the ESPs and 77% across the scrubbers. Particulate sulfate emissions after scrubbing accounted for about 50% by weight of total particulate emissions. The two liquid streams discharged from the site showed concentrations of Al, Ca, Cd, Fe, Mn, Ni, P, and Pb at levels of potential environmental concern. However, in most cases, the levels discharged to the river were not significantly different from those found in makeup water from the river. Waste solids consisted of three collected ash streams and scrubber filter cake. The ashes contained several elements of potential health and ecological concern but few organics (0.04-0.48 mg/kg).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Dust	Pollution Control	13B	11G
Coal	Aerosols	Stationary Sources	21D	
Combustion	Sulfur Oxides	Environmental Assessment	21B	07B
Boilers	Electrostatic Precipitators		13A	
Assessments		Particulate	14B	13I
Flue Gases		Dual-alkali System		
Desulfurization			07A, 07D	

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ABSTRACT

A comprehensive multimedia emissions assessment was performed on a coal-fired boiler equipped with electrostatic precipitators and a dual alkali flue gas desulfurization system. Levels 1 and 2 sampling and analysis procedures were used to characterize pollutant emissions in gaseous, liquid, and solid waste streams. Flue gas pollutant concentrations were measured at the inlet and outlet of both control devices.

Flue gas emissions after scrubbing had the following criteria pollutant loadings: 273 ng/J SO_2, 419 ng/J NO_x (as NO_2 at 88% load), 39 ng/J CO, 7.46 ng/J total particulate, 3.8 to 4.3 ng/J total organics, and <0.3 pg/J lead. Scrubbing efficiency for SO_2 was 88%. Particulate removal efficiencies were 99.7% across the electrostatic precipitators and 19% across the scrubbers for a total removal efficiency of 99.86%. Particulates (exclusive of sulfuric acid aerosol) less than 3 μm in diameter accounted for 59% by weight of total particulate emissions. Emissions of primary sulfates averaged 6.6 ng/J, or 2% of total sulfur species emitted. Primary sulfate removal efficiencies were 48% across the ESP and 77% across the scrubber. Particulate sulfate emissions after scrubbing accounted for approximately 50% by weight of total particulate emissions, with about 10% of this particulate sulfate ascribed to entrainment of scrubber liquor. Elements in stack emissions which may be of environmental concern include arsenic, chromium, and iron. Specific anion analyses for nitrate, chloride, and fluoride showed these emissions averaged 0.0018, 0.175, and 0.122 ng/J, respectively. Neither chloride nor fluoride emissions appeared to pose a health hazard. Numerous compounds of polycyclic organic matter were identified in the air emission. Phenanthrene was present at the highest concentration, but was not deemed to pose a significant health hazard.

The two liquid streams discharged from the site showed concentrations of Al, Ca, Cd, Fe, Mn, Ni, P, and Pb at levels of potential environmental concern. However, in most cases, the levels discharged to the river were not significantly different from those found in make-up water obtained from the river. Only calcium content increased appreciably from make-up to discharge. Total organic content of the discharges ranged from 0.002 to 0.290 mg/l.

Waste solids consisted of three collected ash streams and scrubber filter cake. The ashes contained several elements of potential health and ecological concern including Al, As, Ca, Fe, and Mn, but few organics (0.04-0.48 mg/kg). Filter cake contained more organics (19.22 mg/kg), but fewer elements appeared to be of environmental concern.

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1. INTRODUCTION

Conventional combustion processes provide the bulk of the energy consumed in this country, and will continue to be important sources of energy production. Most conventional combustion processes emit and/or discharge potentially harmful pollutants to the environment, and therefore, pose problems in the control of emissions and disposal of wastes. In recognition of these problems, IERL-RTP established the Conventional Combustion Environmental Assessment (CCEA) program to conduct comprehensive assessments of the effects of combustion-related pollutants on human health, ecology, and the environment. These assessments will result in recommendations for control technology and standards development to control adverse effects within reasonable limits.

This report details the results of one such assessment, performed on the Cane Run No. 6 utility boiler operated by Louisville Gas and Electric Co. The unit is a tangentially-fired dry bottom boiler with a gross peak generating capacity of 300 MW. High slagging bituminous coal is normally fired in the boiler. Particulate control is provided by electrostatic precipitators. Sulfur dioxide control is provided by a dual alkali flue gas desulfurization system, which was selected by EPA as a demonstration plant for dual alkali technology.

Samples of flue gas before and after controls and of various liquid and solid process streams and wastes were analyzed. Gas stream analyses were performed for criteria pollutants, sulfur compounds, organic and inorganic species, and particulate size distributions. Water quality parameters were determined for liquids, and organic and inorganic analyses were performed on liquids and solids. Where possible, the results have been interpreted in terms of process operating parameters and environmental impacts.

2. SUMMARY AND CONCLUSIONS

Flue gases, liquids, and solids from a coal-fired utility boiler were characterized as part of a multimedia emissions assessment conducted during December 1979. Gases at the inlet and outlet of control devices were sampled, as well as process and waste liquids and solids. Figure 1 is a simplified process flow diagram showing emission streams and sampling locations.

Level 1 flue gas sampling was conducted with the boiler operating at a constant load of 265 MW (gross), 88% of maximum capacity. Subsequent tests were performed while the boiler operated at lower loads which fluctuated from 170 to 249 MW. Approximately 30% excess air was used to combust the coal which, based on several analyses, was quite variable over the course of the test program. During Level 1 tests, one of the oil reheaters in the scrubber system was not in operation. Observations indicated that poor combustion conditions were common in one of the reheaters during the entire test period. On some Level 2 test days, the scrubber system was operated in a so-called acid cleaning mode which resulted in reduced sulfur dioxide removal. This clouded interpretation of Level 2 sulfur species analyses.

Flue gas emissions are summarized in Table 1. Sulfur emissions data indicate an SO_2 scrubbing efficiency of 88%. Primary sulfate removal efficiencies were 48% across the ESP and 77% across the scrubber. Particulate sulfate emissions after scrubbing accounted for approximately 50% by weight of total particulate emissions, with about 10% of this particulate sulfate ascribed to entrainment of scrubber liquor.

Oxides of nitrogen were determined at 88% boiler load. These emissions averaged over 400 ng/J, which is considered high relative to other sources of this type.

Carbon monoxide data showed high variability. A 100% increase in average emissions (from 19 ng/J to 39 ng/J) was experienced across the scrubber. The increase can be attributed to poor combustion conditions in the oil reheaters.

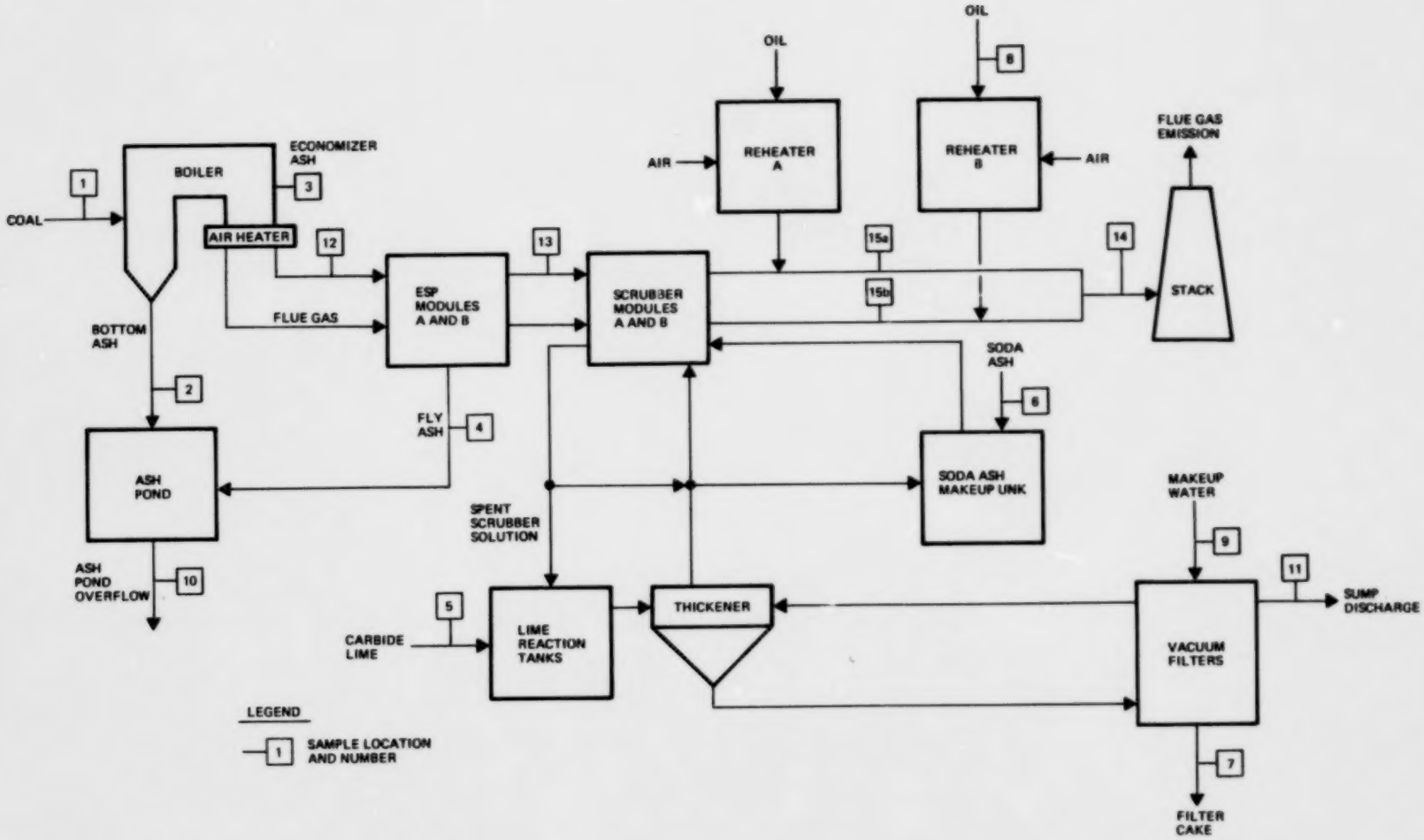

Figure 1. Simplified Process Flow Diagram of Cane Run No. 6

TABLE 1. AVERAGE FLUE GAS EMISSIONS

Pollutant	Emission Factor, ng/J		
	ESP Inlet	ESP Outlet	Scrubber Outlet
SO_2*	2270 ± 250†††	2250 ± 240	273 ± 75
Primary Sulfate†	56	29	6.6
NO_x (as NO_2 at 88% load) ‡	408 ± 25	404 ± 13	419 ± 25
CO**	19 ± 20	19 ± 20	39 ± 15
Total Particulate††	3260	9.20	7.46
Total Organics‡‡	0.87 - 1.4	1.8 - 2.3	3.8 - 4.3
NO_3^-††	0.0126 - 0.0359	0.0016	0.0018
Cl^-***	2.88	2.98 ± 0.60	0.175 ± 0.065
F^-***	4.26	3.37 ± 0.81	0.122 ± 0.017

*SO_2 was determined by pulsed fluorescence (Level 2).

†Primary sulfate (SO_3 as sulfate plus particulate sulfate) data are best estimates based on combined data obtained with the CCS, SASS, and MRI impactor.

‡NO_x was determined by chemiluminescence (Level 1).

**CO was determined by non-dispersive infrared (NDIR) analysis (Level 1).

††Total particulate was determined with the SASS (Level 1). Nitrate was determined by extraction of the SASS particulate catch (Level 2).

‡‡C_1- C_{16} fractions were determined by gas chromatography, while $>C_{16}$ fraction was determined gravimetrically (Level 1).

***Chloride and fluoride were determined with the CCS (Level 2).

†††Data expressed as $\bar{x} \pm s$ are mean ± one standard deviation.

Total particulate data indicated an ESP removal efficiency of 99.7%. A further reduction of 19% is made by scrubbing. At the ESP inlet, 53% by weight of the particulate was larger than 10 μm, 29% was 3-10 μm, 17% was 1-3 μm and 1% was smaller than 1 μm. At the ESP outlet, 9% of the particulate was larger than 10 μm, 15% was 3-10 μm, 49% was 1-3 μm, and 27% was smaller than 1 μm. Of the particulate emissions to the atmosphere, 41% were larger than 3 μm, while 59% were less than 3 μm in diameter. Size distribution data obtained with an MRI impactor indicate that about 70% of the particulate (including H_2SO_4 aerosol) emissions to the atmosphere were less than 1 μm in diameter and capable of deep lung penetration.

Total organic emissions at the scrubber outlet ranged from 3.8 to 4.3 ng/J, and were composed primarily of C_1-C_6 organics. As with some other pollutants, organic emissions increased across the scrubber, most likely due to inputs from the oil-fired reheaters. Polycyclic organic matter (POM) was found to some extent in all three flue gas streams, but was by far most prevalent at the scrubber outlet. Phenanthrene had the highest concentration (37 $\mu g/m^3$) of the seventeen compounds of POM found at the scrubber outlet, and had the highest discharge severity, 0.023.

Inorganic elemental analyses indicated at least 17 elements exceeded their respective Discharge Multimedia Environmental Goal (DMEG)* levels at the ESP inlet, while only four elements exceeded their DMEG levels at the ESP outlet. Scrubber outlet data showed that only arsenic, chromium, and iron exceeded their DMEG values, and may be of environmental concern.

Specific anion analyses indicated emission levels of NO_3^-, Cl^-, and F^- were 0.0018, 0.175, and 0.122 ng/J, respectively. DMEG values have not been established for NO_3^-. Concentrations of Cl^- and F^- did not exceed their respective DMEG values at the scrubber outlet. Hence, these specific anions did not appear to pose a health hazard with short term direct exposure.

Liquid streams analyzed included two streams which were discharged to a river: ash pond overflow and liquid from a sump in the scrubber circuit. In general, the elements posing the greatest environmental concern in these discharges (Al, Ca, Cd, Fe, Mn, Ni, P, and Pb) are all present at similar concentrations in make-up water from the river. Calcium concentration

* For background and charts for DMEGs, see EPA-600/7-77-136 and EPA-600/7-79-176.

increased in the pond discharge relative to the make-up because lime scrubber wastes from other units at the generating station were disposed of in the ash pond. Organic content of the sump discharge was 0.283-0.290 mg/l and was 0.002 to 0.011 mg/l in the ash pond overflow. Traces of naphthalene were also found in the sump discharge.

Solid wastes include fly ash, economizer ash, bottom ash, and scrubber filter cake. The ashes contained three or four elements at concentrations exceeding health-based DMEG values and numerous elements exceeding ecology-based DMEG values. Elements of primary concern from a health standpoint included Al, As, Ca, Fe, and Mn. Filter cake exceeded health-based DMEG values for Ca and Fe, and numerous ecology-based DMEG values. Organics were present at the highest concentration in the filter cake (19.22 mg/kg), and included naphthalene, phenanthrene, and eleven other compounds of polycyclic organic matter.

3. SITE DESCRIPTION

Louisville Gas and Electric Co. (LG&E) owns and operates the Cane Run generating station, located in Jefferson County, Kentucky, about 13 km southwest of Louisville on the south bank of the Ohio River. The power station is comprised of six coal-fired generating units with a total peak capacity of 1040 MW. Unit No. 6, a tangentially-fired dry bottom boiler equipped with electrostatic precipitators (ESPs) and a dual alkali flue gas desulfurization (FGD) system, was tested in this program.

3.1 FUEL

Cane Run No. 6 normally fires Western Kentucky No. 9, a high slagging Eastern Bituminous coal, which limits the time the unit can operate at high load. The coal is quite variable, as shown by the ultimate analysis data in Table 2 (Reference 1).

TABLE 2. TYPICAL ULTIMATE ANALYSIS OF COAL AT CANE RUN NO. 6 (DRY BASIS)

	Typical Analysis, %	Range, %
Carbon	67.15	64.0 - 70.0
Hydrogen	4.72	4.3 - 5.25
Nitrogen	1.28	0.06 - 1.5
Chlorine	0.04	0.03 - 0.06
Sulfur	4.81	3.5 - 6.33
Ash	17.06	15.5 - 24.5
Oxygen	4.94	3.8 - 6.2
Moisture	8.95	8.0 - 10.75
Heat Content, kJ/kg	25,600	22,100 - 28,800 Maximum 24,200 - 27,700 Normal

Coal is delivered by rail and is unloaded either in coal bunkers or a single stock pile. Bunkers for Unit No. 6 hold coal sufficient for about 30 hours of operation, based on the unit's maximum firing rate. Raw crushed coal is delivered from the bunkers to six gravimetric mill feeders which control feed rates to five bowl mills. The pulverized coal is directed to a classifier, and a small tramp iron and foreign material stream is discharged separately from each mill to the bottom ash hopper.

3.2 BOILER

Louisville Gas and Electric Company's Cane Run No. 6 is a 300 MW gross peak capacity tangentially-fired, dry bottom boiler developed by Combustion Engineering. It was placed in service in 1969. It is nominally rated at 280 MW and has a continuous rating of 300 MW. Its minimum controllable rating is 60 MW, and its annual average load has been about 180 MW.

The furnace of Cane Run No. 6 is tangentially-fired mainly by five elevations of coal burners located near the furnace corners. This arrangement directs the fuel streams to imaginary firing circles in the center of the furnace in order to produce efficient mixing of fuel and air. Pulverized coal and primary air are delivered at about 82^{o}C from the classifiers to the burners.

Air and feed streams may be vertically adjusted by means of movable air deflectors and nozzle tips. The furnace is also equipped with warm-up gas and oil guns, igniters, flame scanners, and main gas torches.

Cane Run No. 6 is a dry bottom boiler. Ash and slag from the furnace is discharged through the bottom into two ash hoppers below. The hoppers are emptied by water sluicing to the ash pond for about one hour in each eight hour shift. The ash pond also receives ash and lime scrubber sludge from units 4 and 5 at the Cane Run station.

3.3 ELECTROSTATIC PRECIPITATORS

Cane Run No. 6 is equipped with two single-stage Buell electrostatic precipitators. The ESPs are installed in a cold side configuration (downstream of the air preheaters). Gaseous combustion products pass out of the furnace of the boiler through the economizer and heat the incoming boiler

feed water. The flue gas is then split into two parallel streams. Each stream passes through an air preheater and then through a single-stage electrostatic precipitator. Design efficiency of the precipitators is 99.4 percent. Other design specifications are presented in Table 3.

3.4 DUAL ALKALI FGD SYSTEM

The EPA selected the dual alkali FGD process developed by Combustion Equipment Associates, Inc. (CEA) and Arthur D. Little, Inc. (ADL) as the demonstration plant for dual alkali technology. Construction at Cane Run No. 6 began in 1977, and the system started up in October 1978. Two absorber trains are operated in parallel, fed with gas from the two ESPs.

The CEA/ADL dual alkali system involves absorption of sulfur dioxide using an aqueous solution of alkaline sodium salts. The spent absorbent solution is regenerated using carbide lime, and a solid waste of calcium-sulfur salts is produced. This process is capable of sulfur dioxide removal efficiencies in excess of 95 percent over any range of inlet sulfur dioxide concentration in coal-fired utility boiler applications. The system is also highly effective in removing chlorides from the flue gas. Appropriate selection of scrubbers can enhance particulate removal.

The system is closed loop; the only direct process waste is a washed filter cake of calcium-sulfur salts. No other liquid or solid process streams are discharged.

The CEA/ADL dual alkali FGD process is conveniently considered as three subsystems: gas scrubbing, absorbent regeneration, and solids dewatering. For simplicity, the following description will focus on only one of the two identical trains, Module A.

3.4.1 Gas Scrubbing

Each train in the scrubbing subsystem consists of a countercurrent tray tower absorber (scrubber) equipped with a liquid entrainment separator, an enclosed recycle tank, and recycle pumps.

Flue gas from the electrostatic precipitator (Stream 13) is forced by booster fan through the scrubber. The gas passes upward through sprays, two trays, and finally chevron demisters. The scrubbed flue gas leaving the tower (Stream 16) is mixed with hot gas from an oil-fired reheater (Stream 17) before entering the stack.

TABLE 3. CANE RUN NO. 6 PRECIPITATOR DESIGN SPECIFICATIONS*

Flow Rate	263 m^3/s
Temperature	436 K
Removal Efficiency	99.4%
Rate Constant	2.0 m/s
Plate Area	7191 m^2
Treatment Length	9.5 m
# Fields	3
# Ducts	48 (@ 0.23 m)
Wire Length, meters	15,800 (@ 0.21 m)
Treatment Time	4.2 sec
Delivery	September 1968
# Plate Rappers	36
# Wire Vibrators	9
# Bus Sections	9
Plate Height	9.1 m
Energization	Unfiltered full wave or double half wave
# Ash Hoppers	6

*Two Buell Norblo units are utilized in parallel. Tabulated specifications are for each unit.

Liquor fed to the top tray of the scrubber (Stream 18) passes across the trays and down the tower, and collects at the bottom of the unit where it is mixed with sodium carbonate makeup solution (Stream 25). The spent liquor (Stream 19), having absorbed sulfur dioxide from the gas, contains sodium sulfite and bisulfite. Some of this spent liquor is recycled to the sprays and some to the top tray for pH control. The rest (Stream 20) is sent to the absorbent regeneration subsystem.

3.4.2 Absorbent Regeneration

The spent scrubber solution (Stream 20) which is continuously bled from the scrubber recycle stream is sent to the absorbent regeneration subsystem. Here, the solution is reacted with hydrated lime (Stream 5) in a series of two lime reaction tanks. The lime reduces the acidity of the bisulfite in the scrubber bleed, and converts sodium sulfite and sodium sulfate to sodium hydroxide. These reactions precipitate a mixture of calcium sulfate and calcium sulfite solids.

Slurry from the lime reaction tanks (Stream 21) is sent to a thickener. Overflow from the thickener (Stream 22) is sent back to the scrubbers, and the underflow (Stream 23) is sent to the solids dewatering subsystem.

3.4.3 Solids Dewatering

Slurry from the lime reaction tanks (Stream 21) is fed to the center well of the thickener. Thickener underflow (Stream 23) is dewatered on rotary drum vacuum filters. Filter cake is washed by a series of water sprays which remove most of the occluded soluble sodium salts from the cake. This filtrate (Stream 24) is sent back (via the thickener) to the scrubbing subsystem, conserving sodium values. Solids dewatering produces the only process waste stream from the scrubbing system, the washed filter cake (Stream 7). A small volume liuqid discharge (Stream 11) is also produced in this subsystem. Termed sump No. 6 discharge, Stream 11 consists of condensate collected from vacuum pump silencers.

3.5 SAMPLING LOCATIONS

Sample acquisition points and stream numbers are indicated in Figure 2, and a listing of samples acquired in presented in Table 4.

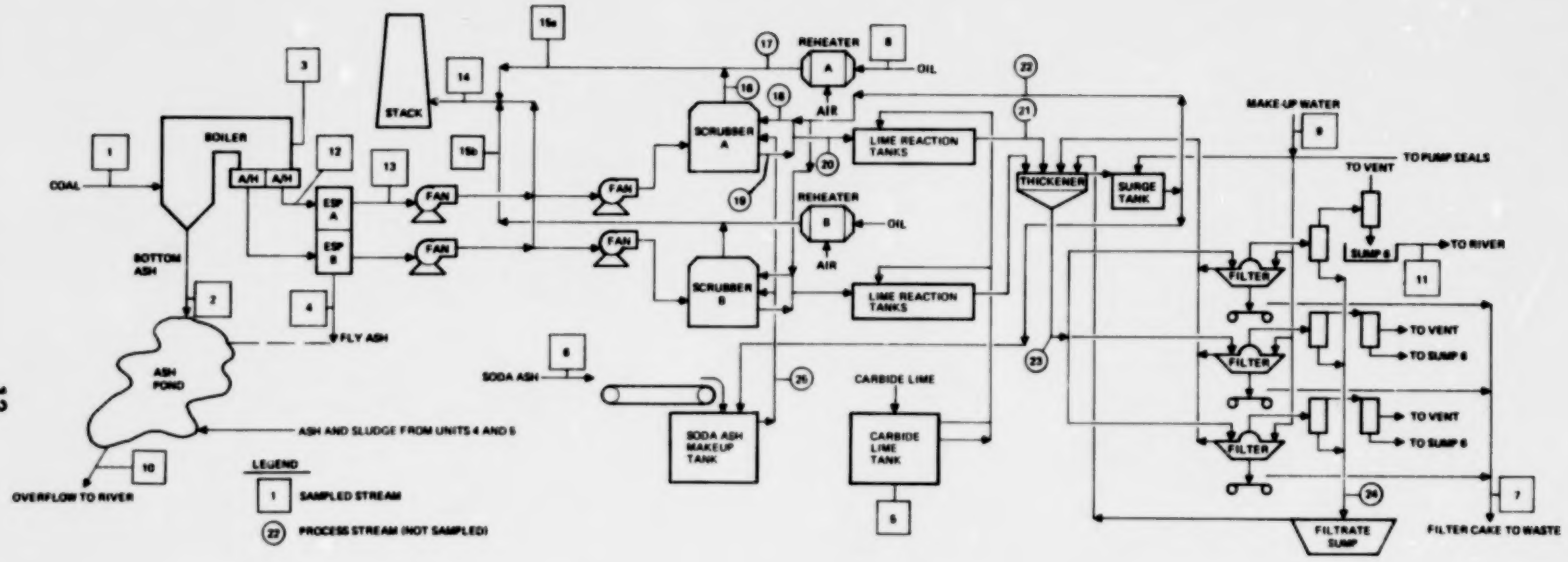

Figure 2. Schematic of Cane Run No. 6

TABLE 4. CANE RUN NO. 6 SAMPLE LISTING

Sample Location*	Sample Number*	Description
1	167/9-16-PB	Coal feed
2	167/9-22-AR	Bottom ash
3	167/9-15-AR	Economizer ash
4	167/9-12-AR	Fly ash
5	167/9-21-AR	Carbide lime
6	167/9-13-AR	Soda ash
7	167/9-14-AR	Filter cake
8	167/9-4-PB	Reheat oil
9	167/9-1-1	Makeup water
2	167/9-22-1	Bottom ash liquid
10	167/9-2-1	Ash pond overflow
5	167/9-21-1	Lime liquid
11	167/9-3-1	Sump No. 6 discharge
12	167	Flue gas, ESP inlet, Module A
13	168	Flue gas, ESP outlet, Module A
14	169	Flue gas, stack
15a/15b	169	Flue gas, scrubber outlet

*Sample location designations are from Figure 1. Sample numbers are TRW internal designations.

4. EMISSIONS ASSESSMENT

Multimedia emission tests were conducted on Unit No. 6 at the LG&E Cane Run station from December 4 through 16, 1979. Gaseous, liquid, and solid process streams and effluents were sampled and analyzed using both Level 1 and Level 2 techniques. This section summarizes plant operating conditions during the test, describes the tests performed, and presents and evaluates test results.

4.1 TEST CONDITIONS

Boiler operating conditions during the test period are summarized in Table 5. During Level 1 testing, 12-6 and 12-7, boiler load remained fairly constant at about 265 MW, or 88% of maximum load. After Level 1 testing was completed, acceptance testing of the scrubber by the utility and its contractors was discontinued. Boiler load was not maintained at a constant level during subsequent tests, and fluctuated from 170 to 249 MW. Fuel feed rates for the first four test days ranged from 86,980 to 99,710 kg/hr. The tabulated feed rates represent the arithmetic average of two measurements; one from a coal feed rate indicator in the boiler control room and the other based on coal totalizer data. Feed rates from 12-10 through 12-16 were estimated using boiler load and the mean feed rate to load ratios determined for 12-4 through 12-7 (351.9 kg/MW-hr). Overall efficiency, computed from gross electrical output and coal feed rate and heating value, averaged about 42%. Boiler oxygen concentration ranged from 4.1 to 5.3%, corresponding to operation at about 30% excess air. Flue gas flow rates were computed from fuel feed rate and ultimate analysis using the following equation:

$$n_{FG} = \frac{4.762\,(n_C + n_S + 0.45\,n_N) + 0.9405\,n_H - 3.762\,n_O}{1 - 0.04762\,[O_2]}$$

where:

n_{FG} = gram moles of dry flue gas per gram of dry coal,
n_i = gram moles of element i per gram of dry coal,
$[O_2]$ = oxygen concentration in the flue gas, volume percent.

TABLE 5. SUMMARY OF TEST CONDITIONS

Test Date	Gross Electrical Output, MW	Percent of Maximum Load	Fuel Feed Rate,* kg/hr	Steam Production Rate, 10^5 kg/hr	Overall Efficiency,† Percent	Boiler O_2, Percent	Estimated Excess Air at Furnace, Percent	Flue Gas‡ Flow Rate, dscm/s
12-4	264	88	99,710	6.58	39.0	4.4	29	230
12-5	261	87	86,980	6.44	44.2	4.1	27	200
12-6	266	89	88,880	6.67	44.1	4.6	31	210
12-7	265	88	97,140	6.58	40.2	4.4	29	230
12-10	249	83	87,610	No data	NM	No data	No data	No data
12-11	170	57	59,810	No data	NM	4.3	28	140
12-13	224	75	78,810	No data	NM	5.3	37	190
12-14	213	71	74,940	No data	NM	4.2	28	170
12-15	227	76	79,860	No data	NM	No data	No data	No data
12-16	191	64	67,200	No data	NM	No data	No data	No data

* Calculated based on an arithmetic average of two types of measurement for 12-4 through 12-7. Thereafter, rates are estimated using boiler load, and ratio of boiler load to feed rate from earlier tests on 12-4 through 12-7.

† Since coal feed rates for tests on and after 12-10 were estimated from boiler load, efficiencies calculated from these feed rates are not meaningful (NM).

‡ Flue gas flow rates are based on boiler O_2 levels and fuel feed rates. Thus, flow rates for 12-11, 12-13, and 12-14 are estimates based on approximate fuel feed rates.

Flue gas flow rates are expressed as dry standard cubic meters (dscm) per second based on boiler oxygen levels. Standard conditions are 20°C and 101.3 kPa. Note that flue gas flow rates change from one part of a process to another due to air leaking into the system. The leakage is taken into account by the $[O_2]$ term.

Table 6 is a summary of proximate and ultimate coal analyses. Analyses of samples taken by TRW are compared to those taken by Bechtel during FGD acceptance testing. As noted in Section 3, the coal burned at Cane Run is highly variable in composition. Moisture content varied widely, while chlorine, sulfur, and nitrogen contents also showed substantial variability within the course of only two days. Coal nitrogen is not only variable but is present at a somewhat higher concentration than is typical for bituminous coal. Elemental analyses of the TRW coal sample are presented in Table 7.

4.2 TESTS AND FIELD ANALYSES

A combination of laboratory and field analyses, as required, were performed on gaseous, liquid, and solid samples obtained during emission testing. This section summarizes the sampling/analysis methodology used. Both Level 1 and Level 2 sampling and/or analysis procedures were used at Cane Run. Details of the Level 1 (or modified Level 1) procedures have been documented elsewhere (2). Level 2 methods and procedures specific to this test are detailed in Appendices A and B of this report.

4.2.1 Gas Streams

Table 8 is a schedule of flue gas testing. The bulk of the Level 1 sampling was performed with the Source Assessment Sampling System (SASS) which was used to collect gaseous and fine particulate emissions at the ESP inlet, ESP outlet, and scrubber outlet. The SASS train is illustrated in Figure 3. The train consists of a heated probe, followed by three cyclones and a filter, enclosed in a heated oven, for particulate measurements. Gaseous flue gas components are trapped in the remainder of the train, which consists of a gas conditioner, an XAD-2 polymer absorbent trap and a series of impingers. The XAD-2 traps primarily organics, and some inorganics, while the impingers collect the remaining inorganic constituents of the flue gas to be measured. All sample contact surfaces are Type 316 stainless

TABLE 6. SUMMARY OF COAL ANALYSES*

Component	Date			Variation	
	12-5†	12-7†	12-7‡	Mean	s(x)
Moisture, %	4.28	4.04	10.57	6.30	3.70
Ash, %	15.18	15.52	17.43	16.04	1.21
Volatile, %	37.70	No data	35.44	36.57	--
Fixed Carbon, %	47.12	No data	47.13	47.13	--
Total Carbon, %	66.13	67.34	65.70	66.39	0.85
Hydrogen, %	4.54	4.54	4.55	4.54	0.006
Nitrogen, %	1.49	1.57	1.92	1.66	0.23
Chlorine, %	0.07	0.07	0.02	0.05	0.03
Sulfur, %	4.77	3.25	3.37	3.80	0.85
Oxygen, %	7.82	7.71	7.01	7.51	0.44
Heating Value, kJ/kg	11,853	12,152	11,749	11,918	209

*All analyses are reported on a dry basis except fuel moisture. Oxygen concentrations are by difference.

†Sampled by Bechtel.

‡Sampled by TRW. This analysis was used to compute emission factors. Other analyses are included to show variability of coal feed.

TABLE 7. ELEMENTAL ANALYSIS OF RAW COAL*

Element	Concentration, µg/g	Element	Concentration, µg/g
Ag	<0.1	La	<0.1
Al	22,800	Li	14
As	<5 (102)†	Mg	60
Au	<0.04	Mn	11.6
Ba	<1	Mo	<3.8
Be	<0.05	Na	803
Ca	32	Ni	70.7
Cd	<0.3	P	282
Ce	<5	Pb	22
Co	<0.4	Sb	<19 (<2)†
Cr	<0.5	Se	<5
Cu	62.6	Si	34,100
Fe	26,000	Sn	<5
Ga	<3	Sr	<3
Ge	7.2	Ti	<0.1
Hg	<1	V	117
K	335	Zn	26.8
		Zr	53

* Elemental concentrations are on a dry basis. Analytical method is ICP (Level 2).

† Additional analytical results for As and Sb were obtained by graphite furnace atomic absorption analysis.

TABLE 8. SCHEDULE FOR FLUE GAS TESTING

Test Date	Location*	Sampling/Analyses Performed: Levels 1 and 2,† Continuous O_2, CO_2, SO_2, CO, NO, NO_x	Level 1, C_1-C_6 Hydrocarbons	Level 1, SASS	Level 1, SASS Bioassay	Level 2, CCS	Level 2, MRI
12-4	ESP Inlet	X					
	ESP Outlet	X					
	Scrubber Outlet	X					
12-5	ESP Inlet	X					
	ESP Outlet	X					
	Scrubber Outlet	X					
12-6	ESP Inlet	X					
	ESP Outlet	X	X	X			
	Scrubber Outlet	X	X	X			
12-7	ESP Inlet	X	X	X			
	ESP Outlet	X	X	X			
	Scrubber Outlet	X	X	X			
12-10	ESP Inlet	X			X		
	ESP Outlet	X			X		
	Scrubber Outlet	X					
12-11	ESP Inlet	X			X		
	ESP Outlet	X			X		
	Scrubber Outlet	X					
12-13	ESP Inlet	X			X		X
	ESP Outlet	X			X		X
	Scrubber Outlet	X					
12-14	ESP Inlet	X			X	X	X
	ESP Outlet	X			X	X	X
	Scrubber Outlet	X					
12-15	ESP Inlet	X			X	X	
	ESP Outlet	X			X	X	
	Scrubber Outlet	X				X	
12-16	ESP Inlet	X			X	X	
	ESP Outlet	X			X	X	
	Scrubber Outlet	X					

*The plant consists of two ESP/scrubber trains in parallel. Sampling and analysis were performed at the "ESP inlet" and "ESP outlet" of train A. For the "scrubber outlet", continuous monitoring and Level 1 SASS bioassay sampling were performed on both trains, at locations 15a and 15b of Figure 1. All other "scrubber outlet" samples were obtained at location 14, after the two parallel streams joined.

†During CCS and MRI testing, only O_2, CO_2, and SO_2 were monitored continuously.

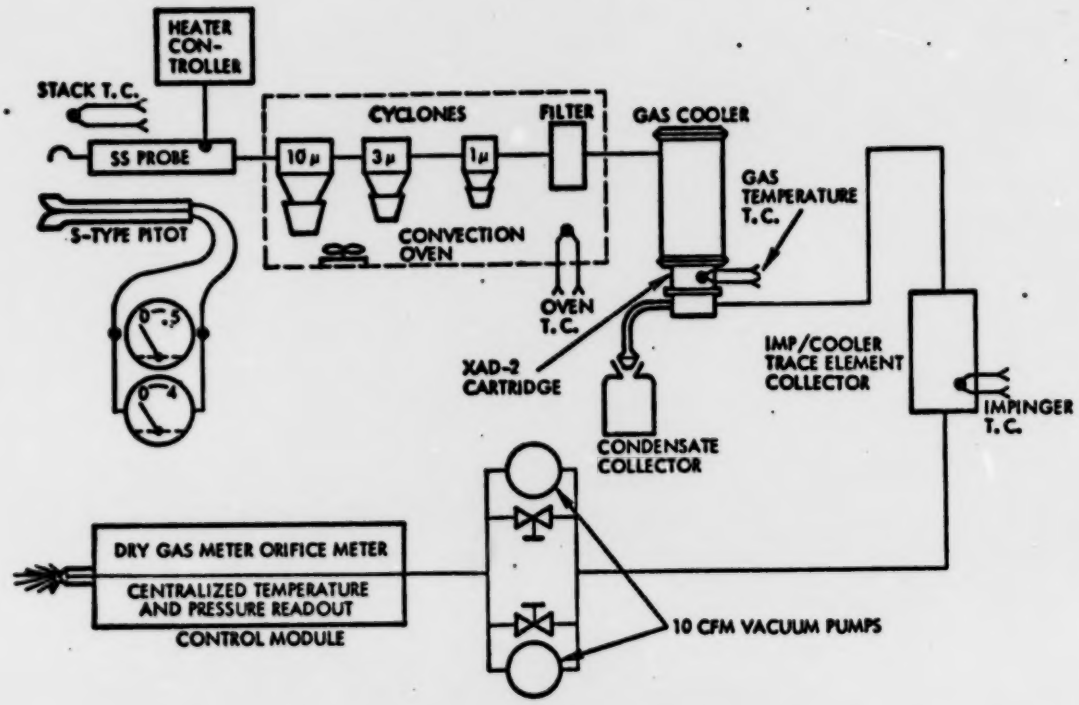

Figure 3. Schematic of the Source Assessment Sampling System (SASS)

steel, glass, or teflon. A 30.28 dscm sample of flue gas was collected at the ESP inlet for Level 1 tests. For the ESP outlet and scrubber outlet, 61.20 and 53.58 dscm samples, respectively, were obtained by compositing SASS catches from 12-6 and 12-7. SASS bioassay samples were obtained at the ESP outlet and scrubber outlet. To provide sufficient sample for bioassay, the SASS train was run simultaneously at the scrubber outlet of both plant modules (A and B).

Integrated bag samples were obtained from each flue gas sampling point during SASS operation. These samples were analyzed in the field to determine the concentrations of C_1-C_6 hydrocarbons. A Shimadzu GC-Mini 1 gas chromatograph with flame ionization detectors was the analytical instrument. Fixed gases, O_2, CO_2, N_2 and CO were also determined in the field from bag samples. A Shimadzu GC-3BT gas chromatograph with thermal conductivity detectors was used.

Continuous monitors were used to obtain data on O_2, CO_2, SO_2, NO, NO_x, and CO at the ESP inlet and outlet, and at the outlet of scrubber modules A and B. With the exception of the NO and NO_x analyses, which are Level 1, all continuous monitoring was performed using Level 2 methods. Table 9 is a list of continuous monitoring equipment used at Cane Run.

Level 2 tests were performed using the Controlled Condensation System (CCS) and MRI impactors. The CCS, illustrated in Figure 4, was used at all sampling locations to sample for SO_2, SO_3 (as H_2SO_4), particulate sulfate, HCl, and HF. MRI impactors were used at the scrubber inlet and outlet to determine changes in particle size distribution across the FGD system.

4.2.2 Liquid Streams

The following liquids and slurries were sampled by tap sampling: make-up water, sump #6 discharge, and carbide lime slurry. Ash pond overflow and bottom ash slurry were grab sampled. Field analyses were performed for temperature, pH, and water quality parameters (hardness, alkalinity, ammonia nitrogen, phosphate phosphorus, sulfate, sulfite, nitrate, and cyanide). Temperature and pH were recorded each day for three days, while water quality analyses were only performed once during the test. All liquid samples were stabilized to pH <2 in the field, prior to laboratory analyses.

TABLE 9. CONTINUOUS MONITORING EQUIPMENT

Gas	Instrument Name	Analytical Method
O_2	Beckman Model 755	Magnetic Susceptibility
CO_2	Infrared Industries Model IR 702	NDIR
SO_2	TECO Model 40	Pulsed Fluorescence
NO	TECO Model 10	Chemiluminescence
NO_x	TECO Model 10	Chemiluminescence
CO	Beckman Model 865	NDIR

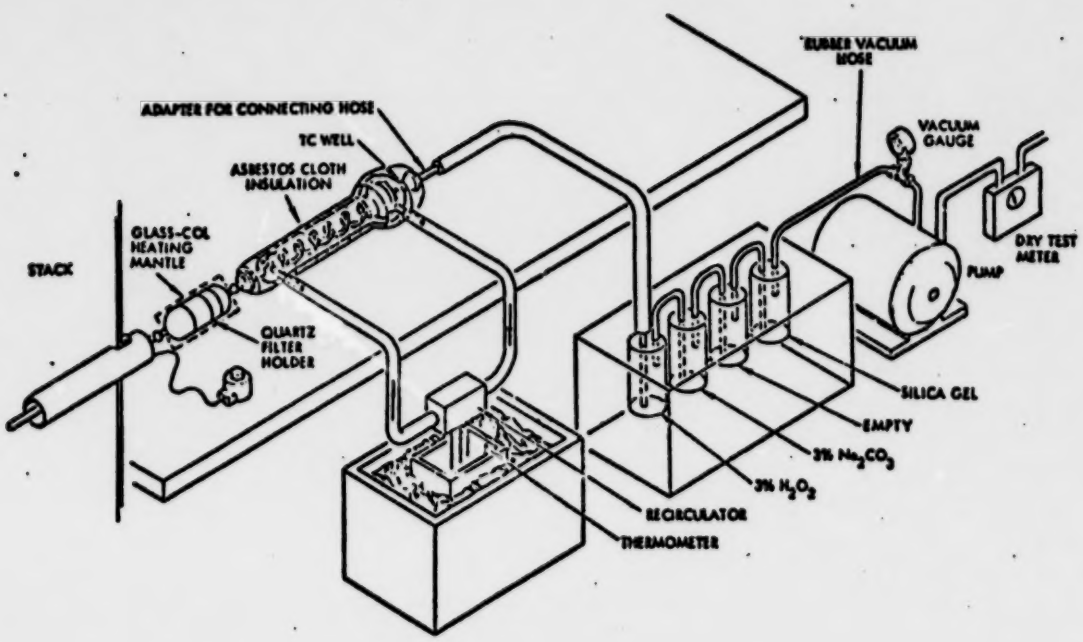

Figure 4. Schematic of Modified Controlled Condensation System (CCS)

4.2.3 Solids

Solid grab samples of ESP fly ash, soda ash, and filter cake were obtained on each of the two SASS Level 1 days and composited. The solid portions of the bottom ash and carbide lime slurries, as well as the reheat oil have been classified under the solids category for analysis and reporting. No field analysis was required for solid samples, however, the solid portion of slurry samples was field dried before shipment to the laboratory.

4.3 LABORATORY ANALYSES

Samples submitted for laboratory analysis were processed through one of four basic analytical schemes: 1) the analytical scheme for particulates and gases; 2) the analytical scheme for solids, liquids, and slurries; 3) the CCS sample analysis scheme; or 4) the MRI impactor sample analysis scheme. The principal elements of these analytical schemes are presented in Figures 5 through 7. Detailed analytical procedures can be found in Reference 2.

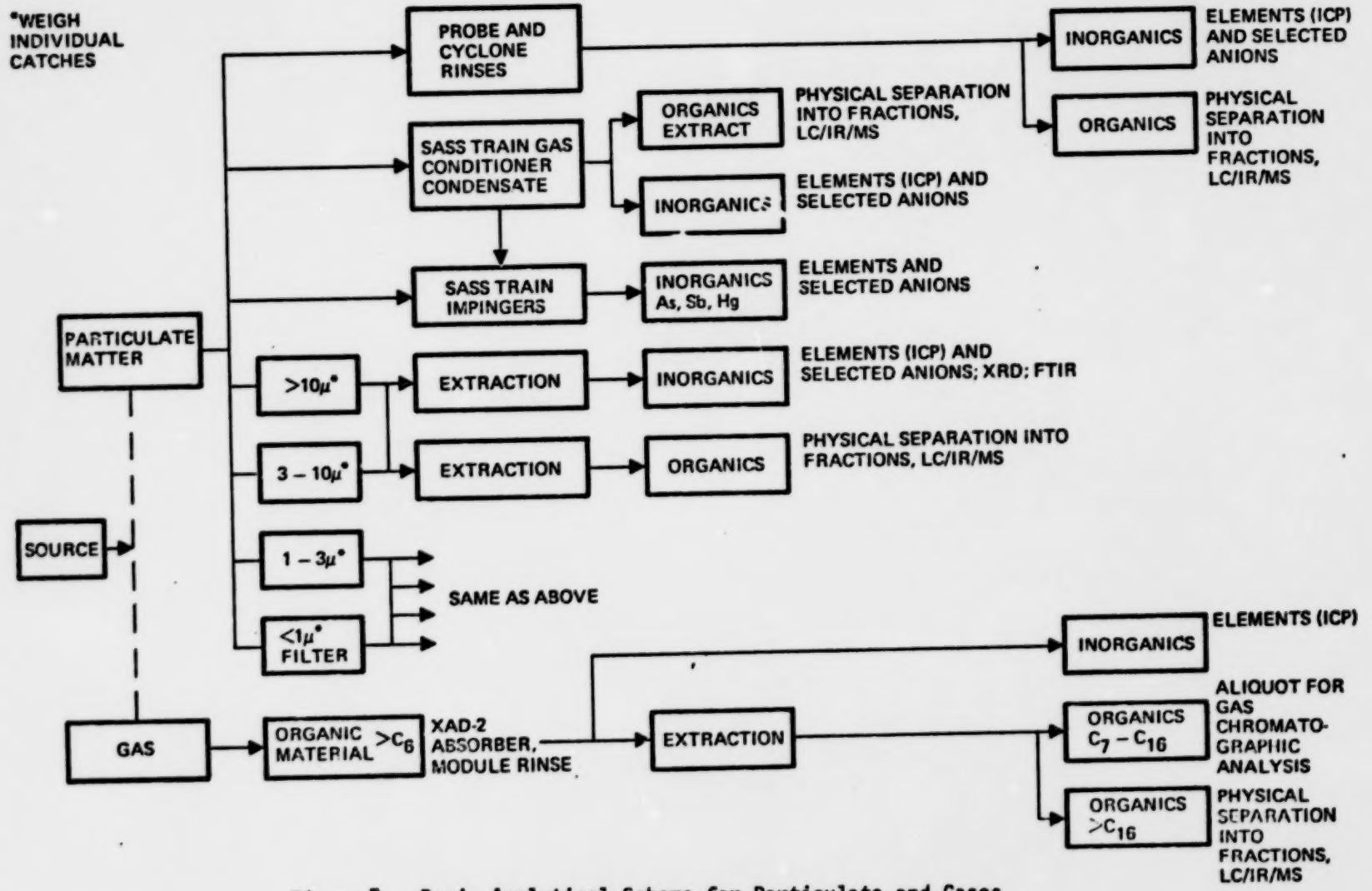

Figure 5. Basic Analytical Scheme for Particulate and Gases

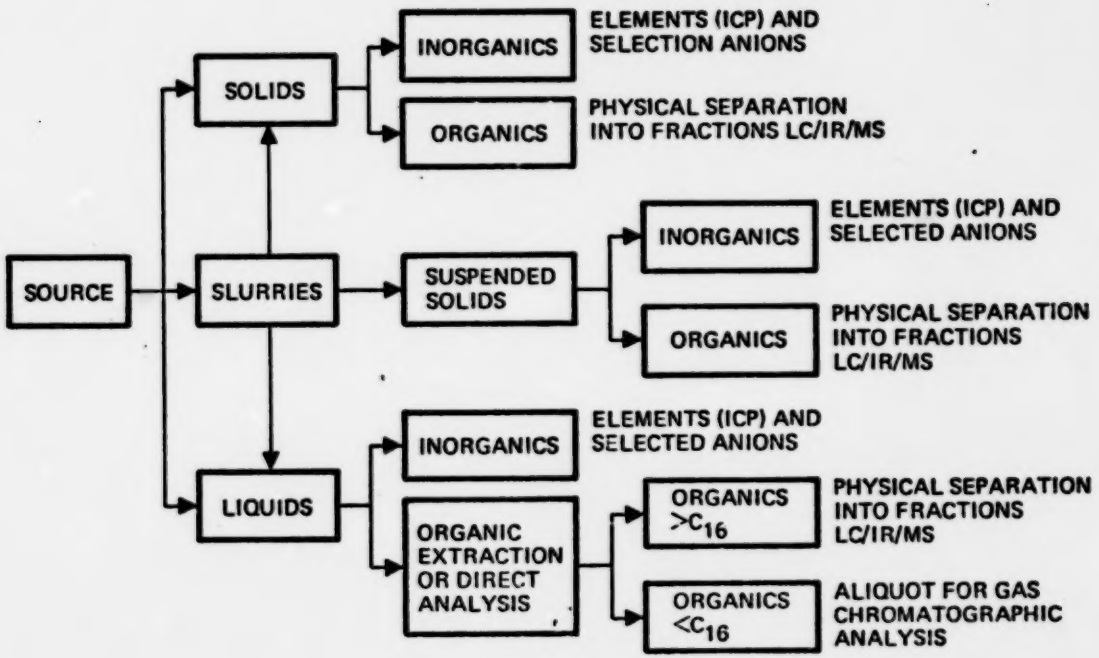

Figure 6. Basic Analytical Scheme for Solids, Slurries, and Liquids

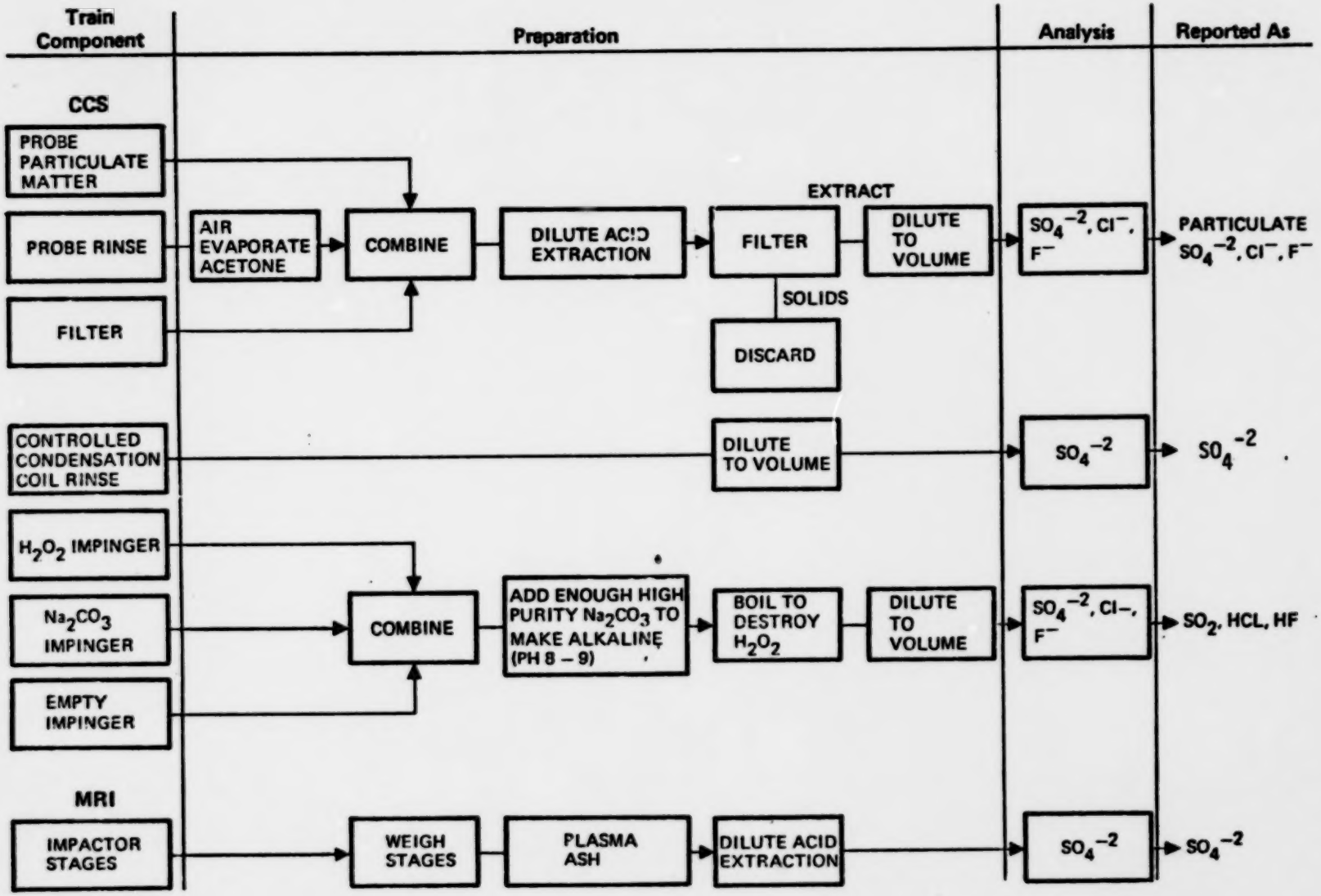

Figure 7. Basic Analytical Scheme for CCS and MRI Impactor Samples

A discussion of procedural modifications specific to this test effort is presented in Appendices A and B.

Inductively Coupled Optical Emission Spectroscopy (ICP) was used for most trace element determinations. This Level 2 method was chosen over the standard Level 1 method, Spark Source Mass Spectrometry (SSMS). The reason for this choice was that ICP can more accurately measure most of the elements of environmental concern which have been identified previously by SSMS screening on other coal-fired boilers.

4.4 FLUE GAS EMISSIONS

4.4.1 Criteria Pollutants*

Table 10 is a summary of criteria pollutant measurements made at Cane Run during the test period. Daily average criteria pollutant emissions are presented in Table 11. Finally, average uncontrolled emissions are compared with EPA AP-42 emission factors for uncontrolled sources (3) in Table 12. Emissions data are discussed by specific pollutant in the following subsections.

Sulfur Dioxide--

Uncontrolled SO_2 emissions were measured in the range of 1796 to 2591 ng/J, and averaged 2270 ng/J at the ESP inlet and 2250 ng/J at the ESP outlet. These values compare favorably to the AP-42 value of 2300 ng/J. They are also in good agreement with a computed SO_2 emission factor of 2420 ng/J based on fuel analyses and an assumed 98 percent conversion of fuel sulfur to SO_2.

Average SO_2 emissions at the scrubber outlet were 273 ng/J, corresponding to a removal efficiency of 88 percent across the FGD system. Scrubber outlet SO_2 data for 12-10, 12-15, and 12-16 were not used in computing the average emissions or removal efficiency. During tests on these days the FGD system was being operated in so-called acid cleaning mode. Acid cleaning is a procedure that was used to alleviate a water balance problem in the scrubbing system. Lime slurry feed was entering the process at less than 20% solids, compared to a design specification of 30% (1). This resulted

*Lead, a criteria pollutant, is discussed in a subsequent section of this report.

TABLE 10. AVERAGE CRITERIA POLLUTANT EMISSIONS

Pollutant	Emission Factor, ng/J*		
	ESP Inlet	ESP Outlet	Scrubber Outlet
SO_2	2270 ± 250	2250 ± 240	273 ± 75
NO_x (as NO_2 at 88% load)	408 ± 25	404 ± 13	419 ± 25
CO	19 ± 20	19 ± 20	39 ± 15
Total Particulate	3260	9.20	7.46
Total Organics	0.87 - 1.4	1.8 - 2.3	3.8 - 4.3

*Where applicable data are presented as mean ± one standard deviation.

in dilution of active sodium values in the system. To increase sodium concentration in the scrubbing solution, fresh lime feed to the scrubbers was turned down or off, and only spent scrubber liquor allowed to recycle in the absorber subsystem. As water in the scrubber was carried out of the system with the flue gas, the scrubber liquor became more concentrated and sodium concentration in the scrubber loop increased to an acceptable level. However, since little or no fresh lime was added to the loop, SO_2 removal decreased markedly, and the level of sulfur species in the flue gas increased.

Nitrogen Oxides--

NO_x emissions are a function of boiler load and thus must be stated and compared on that basis. Since load was only held constant for the first four test days, NO_x data were only averaged over this period. Average NO_x levels at 88% load (expressed as NO_2) were 408 ng/J at the ESP inlet, 404 ng/J at the ESP outlet, and 419 ng/J at the scrubber outlet. These levels are in good agreement with each other, but are consistently higher than the AP-42 emission factor of 330 ng/J at full load. The slight increase in NO_x across the scrubber may be due to thermal NO_x formation in the oil reheater. However, the main explanation for the consistently high NO_x levels is probably the high concentration of nitrogen in the feed coal.

TABLE 11. SUMMARY OF CRITERIA POLLUTANT EMISSIONS

Test Date	Sample Location	SO_2	NO_x (as NO_2)	CO	Total* Particulates	C_1-C_6 Organics	C_7-C_{16}* Organics	>C_{16}* Organics	Total Organics
12-4	ESP Inlet	2591	425	4.5	ND†	ND	ND	ND	ND
	ESP Outlet	2541	408	4.5	ND	ND	ND	ND	ND
	Scrubber Outlet	363	441	32	ND	ND	ND	ND	ND
12-5	ESP Inlet	2415	373	11	ND	ND	ND	ND	ND
	ESP Outlet	2379	391	11	ND	ND	ND	ND	ND
	Scrubber Outlet	219	393	36	ND	ND	ND	ND	ND
12-6	ESP Inlet	2263	428	20	ND	ND	ND	ND	ND
	ESP Outlet	2233	421	19	ND	0.59-1.1	ND	ND	ND
	Scrubber Outlet	223	440	38	ND	1.2 -1.7	ND	ND	ND
12-7	ESP Inlet	2106	407	7.6	ND	0.50-1.0	ND	ND	ND
	ESP Outlet	2087	397	5.4	ND	2.0 -2.5	ND	ND	ND
	Scrubber Outlet	251	401	26	ND	2.6 -3.1	ND	ND	ND
12-10	ESP Inlet	1797	376	54	ND	ND	ND	ND	ND
	ESP Outlet	1796	382	53	ND	ND	ND	ND	ND
	Scrubber Outlet	1376	393	64	ND	ND	ND	ND	ND
12-11	ESP Inlet	2140	289	ND	ND	ND	ND	ND	ND
	ESP Outlet	2155	283	ND	ND	ND	ND	ND	ND
	Scrubber Outlet	341	293	ND	ND	ND	ND	ND	ND
12-11	ESP Inlet	2476	ND	ND	ND	ND	ND	ND	ND
	ESP Outlet	2453	ND	ND	ND	ND	ND	ND	ND
	Scrubber Outlet	343	ND	ND	ND	ND	ND	ND	ND
12-14	ESP Inlet	2279	ND	ND	ND	ND	ND	ND	ND
	ESP Outlet	2082	ND	ND	ND	ND	ND	ND	ND
	Scrubber Outlet	172	ND	ND	ND	ND	ND	ND	ND
12-15	ESP Inlet	2082	ND	ND	ND	ND	ND	ND	ND
	ESP Outlet	2183	ND	ND	ND	ND	ND	ND	ND
	Scrubber Outlet	1490	ND	ND	ND	ND	ND	ND	ND
12-16	ESP Inlet	2590	ND	ND	ND	ND	ND	ND	ND
	ESP Outlet	2576	ND	ND	ND	ND	ND	ND	ND
	Scrubber Outlet	1485	ND	ND	ND	ND	ND	ND	ND
Average	ESP Inlet	2270	408**	19	3260	ND	0.072	0.30	0.87-1.4
	ESP Outlet	2250	404**	19	9.20	1.3 -1.8	0.42	0.12	1.8 -2.3
	Scrubber Outlet	273‡	419**	39	7.46	1.9 -2.4	0.37	1.46	3.8 -4.3

* Total particulate and >C_7 organics data are composites obtained from SASS Level 1 runs on 12-6 and 12-7. Daily loadings were not determined.

† No Data.

‡ SO_2 measurements at the scrubber outlet for 12-10, 12-15, and 12-16 were not used in computing the average.

** Average emissions at 88% load. Data for 12-10 and 12-11 were not used in computing the average because load was lower.

TABLE 12. COMPARISON OF UNCONTROLLED CRITERIA POLLUTANT EMISSIONS WITH EPA AP-42 EMISSION FACTORS

Pollutant	Emission Factor, ng/J		
	ESP Inlet	ESP Outlet	AP-42 Emission Factor
SO_2	2270 ± 250	2250 ± 240	2300
NO_x (as NO_2 at 88% load)	408 ± 25	404 ± 13	330
CO	19 ± 20	19 ± 20	30
Total Particulate	3260	9.20*	5400
Total Organics	0.87 - 1.4	1.8 - 2.3	5

*Controlled particulate data are not comparable to AP-42 data.

Continuous monitoring of NO alone was also conducted during tests at Cane Run. Although these data are not reported, they indicate that NO consistently comprised about 96 mole percent of the total oxides of nitrogen present in all flue gas streams.

Carbon Monoxide--

Carbon monoxide emissions at both the ESP inlet and ESP outlet averaged 19 ng/J during the days CO was monitored (12-4 through 12-10). These averages are in excellent agreement with the AP-42 emission factor of 20 ng/J. There is considerable scatter to the measured CO data, however, this is not atypical for coal-fired utility boilers. Higher CO levels were recorded at the scrubber outlet; CO emissions averaged 39 ng/J. This increase can be attributed to the oil-fired reheater on the FGD system. Field observations indicated intermittent poor combustion conditions in the reheater, resulting in some soot production.

Total Particulates--

Total particulates were determined using the SASS train, a Level 1 methodology. One sample was collected at the ESP inlet on 12-7; samples were taken at the ESP outlet and scrubber outlet on 12-6 and 12-7 and composited. The particulate loading measured at the ESP inlet was 3260 ng/J, which is only 60% of the AP-42 uncontrolled emisson factor of 5400 ng/J.

This would indicate that only about 50% of the fuel ash was present as entrained particulate, rather than the 95% indicated by AP-42 for pulverized coal-fired dry bottom utility boilers. Particulate stratification in the flue gas duct is suspected, and could have resulted in a non-representative sample being acquired with the SASS. Duct configuration upstream of the sampling point could not be determined due to the physical layout of the plant, so this conclusion cannot be verified.

Particulate loadings at the ESP outlet and scrubber outlet were 9.20 and 7.46 ng/J, respectively. This represents a particulate removal efficiency of 19% for the scrubber. Based upon the AP-42 uncontrolled emission factor of 5400 ng/J, the overall particulate removal efficiency of the boiler/FGD combination is about 99.86%. Even using the conservative (SASS) value for uncontrolled emissions, overall particulate removal is at least 99.7%.

Total Organics--

Total organic emissions were measured during Level 1 tests on 12-6 and 12-7. Average organic emissions for these days ranged from 0.87 to 1.4 ng/J at the ESP inlet and 1.8 to 2.3 ng/J at the ESP outlet. These levels are well below the 5 ng/J AP-42 emission factor. Stack emissions of total organics were considerably higher than levels measured upstream, owing to inputs from the FGD system oil reheater. Total organics averaged 3.8 to 4.3 ng/J at the scrubber outlet. Organic emissions are discussed in detail in Section 4.4.5.

4.4.2 Particle Size Distribution

Both Level 1 and Level 2 methods were used to obtain particle size distribution data at Cane Run. The SASS train (Level 1) employs cyclonic separation, while the MRI impactor (Level 2) catches particles by inertial impaction. SASS sampling was performed at all three flue gas locations on 12-6 and 12-7, while MRI tests were conducted only at the scrubber inlet and outlet on 12-13 and 12-14.

Data from SASS tests are presented in Table 13. They indicate a decrease in removal efficiency by the ESP and the ESP/scrubber combination

TABLE 13. PARTICLE SIZE DISTRIBUTIONS MEASURED WITH THE SASS*

Aerodynamic Diameter Size Range, μm	Weight Percent			Emission Factor, ng/J			Removal Efficiency, Percent		
	ESP Inlet	ESP Outlet	Scrubber Outlet	ESP Inlet	ESP Outlet	Scrubber Outlet	ESP	Scrubber	Overall
>10†	53.3	8.9	32.6	1740	0.815	2.43	99.95	NM‡	99.86
3-10	28.9	15.2	8.5	940	1.40	0.636	99.85	54.63	99.93
1-3	16.9	48.9	24.2	549	4.50	1.81	99.18	59.81	99.67
<1	0.9	27.0	34.7	29.7	2.49	2.59	91.61	NM‡	91.26
Total	100.0	100.0	100.0	3260	9.20	7.47	99.72	18.89	99.77

* Level 1.

† Includes probe rinse.

‡ Not Meaningful. Particulate loading for these size fractions increased across scrubber.

with decreasing particle size, as expected. The data also show an increase in particulates larger than 10 μm, and less than 1 μm across the scrubber. The increase in large particles is unexpected, and may be due to sampling error. Larger particles are much more subject to segregation than smaller particles. Thus, variations in sampling point and isokinetics will affect the reported values for large particles more than small particles. The increase in small particles (<1 μm) may be attributable to scrubber generated particulate. This point is discussed further below.

Level 2 data from MRI tests are presented in Table 14 for the scrubber inlet and outlet streams. Tabulated D_{50} values are the aerodynamic diameters of particles which will be collected by the specific stage with 50% efficiency. Impactor data at the scrubber inlet show good reproducibility. Particle size distributions determined from the MRI tests agree well with data from the SASS tests, though total particulate loading for the MRI tests was about 20% less than for the SASS tests. This may be due to the fact that ESP rapper repairs were made between Level 1 and Level 2 tests, which could have enhanced ESP collection efficiency.

Impactor data at the scrubber outlet were not as consistent as scrubber inlet data, mainly due to a large filter catch on the second test day. However, during the second test, the FGD unit was operated in acid cleaning mode, which may explain the difference. In general, outlet loadings measured with the MRI impactor are higher than those measured with the SASS. The discrepancy is particularly apparent in the <1 μm size fraction, which, according to the MRI data, comprises about 70% of total particulate. The increased loadings determined by the MRI impactor as compared to the SASS are largely attributable to H_2SO_4 aerosol which is not measured by the SASS. Because flue gas temperatures at the scrubber outlet (about 73°C) are less than the acid dew point (about 127°C), flue gas H_2SO_4 can condense on MRI impactor plates. But the SASS cyclones and filter are operated at 205°C, and so any H_2SO_4 which does not react with ash constituents would be evaporated and hence not measured. Conversely, the MRI impactors were operated at temperatures near the acid dew point so H_2SO_4 impacting the plates would not completely evaporate after impaction. Sulfate analyses from both SASS and MRI measurements support this conclusion.

TABLE 14. PARTICLE SIZE DISTRIBUTION MEASURED WITH THE MRI IMPACTOR*

Scrubber Inlet					Scrubber Outlet				
Test Date	Stage	D_{50}, μm	Particulate Loading		Test Date	Stage	D_{50}, μm	Particulate Loading	
			mg/m^3	ng/J				mg/m^3	ng/J
12-13	1	28.64	0.66	0.26	12-13	1	23.43	0.261	0.135
(6.7% O_2)	2	14.04	1.49	0.592	(9.8% O_2)	2	11.48	0.197	0.102
	3	5.256	4.13	1.64		3	4.284	2.12	1.09
	4	2.389	6.84	2.72		4	1.937	4.39	2.26
	5	1.368	2.18	0.866		5	1.101	2.28	1.18
	6	0.6426	1.56	0.612		6	0.5083	2.44	1.26
	7	0.4241	NP†	--		7	0.3298	NP	--
	Filter	0.2	2.40	0.954		Filter	0.2	7.18	3.70
	Total	--	19.26	7.65		Total	--	18.87	9.73
12-14	1	31.65	NP	--	12-14	1	24.10	0.277	0.124
(6.8% O_2)	2	15.52	0.929	0.369	(8.1% O_2)	2	11.81	0.289	0.130
	3	5.819	2.72	1.08		3	4.407	1.79	0.804
	4	2.652	7.46	2.97		4	1.994	7.31	3.28
	5	1.523	3.90	1.55		5	1.134	3.28	1.47
	6	0.7214	0.794	0.316		6	0.5238	3.43	1.54
	7	0.4800	1.27	0.505		7	0.3401	NP	--
	Filter	0.2	1.10	0.437		Filter	0.2	16.54	7.43
	Total	--	18.17	7.23		Total	--	32.92	13.31

* Level 2.

† No Plate.

4.4.3 Sulfur Compounds

The three sulfur species of interest - SO_2, SO_3, and particulate sulfate - were determined in flue gas emissions by several methods. The CCS was utilized at the ESP inlet, ESP outlet, and scrubber outlet to measure SO_2, SO_3, and particulate sulfate. Particulate sulfate was also determined from SASS and MRI catches by extracting solids collected from these devices. SASS samples were collected at all three flue gas sampling points while MRI samples were only collected at the ESP outlet and scrubber outlet. Continuous monitoring of SO_2 was also performed at all three locations, as described in an earlier section.

SO_2--

Results of sulfur species determinations from the CCS (Level 2) are summarized in Table 15. Data obtained at the ESP inlet on 12-14 and 12-15 were not reliable due to improper positioning of the probe, and were, therefore, not reported. Sulfur species data at the scrubber outlet, particularly SO_2, obtained on 12-15 and 12-16, may not represent normal FGD operation, since the FGD system was being operated in acid cleaning mode on these days. Measurements across the scrubber for 12-14 show 95% SO_2 removal, compared to 92% removal determined from continuous monitoring data. Sulfur dioxide comprised 99.5% of the sulfur species present before scrubbing and 95.2% after scrubbing.

SO_3--

CCS data for SO_3 trend higher each test day. The reasons for this trend become more apparent when boiler operating conditions are examined. Oxygen concentrations at the ESP outlet increased each day during CCS testing, indicating increased boiler oxygen levels. Since increased O_2 concentration in the boiler favors formation of SO_3, this would explain part of the increase in measured SO_3 values. In addition, boiler load was substantially lower on 12-16 than on either 12-14 or 12-15. This would cause combustion temperature to be lower, another factor favoring SO_3 formation. Variations in fuel sulfur may also contribute to day to day variations in SO_3, but this cannot be confirmed. No reduction in SO_3 across the ESP was measured, as expected. SO_3 comprised 0.4 to 1.0% of the total sulfur species in the flue gas at the ESP outlet. CCS data for SO_3 emissions at

TABLE 15. EMISSIONS OF SULFUR SPECIES AS DETERMINED WITH THE CONTROLLED CONDENSATION SYSTEM*

Sulfur Compound	Test Date	Emission Factor, ng/J†			Mole % of Total Sulfur Species in the Flue Gas		
		ESP Inlet	ESP Outlet	Scrubber Outlet	ESP Inlet	ESP Outlet	Scrubber Outlet
SO_2	12-14	No data (2279)	2330 (2082)	108 (172)	No data	99.48	95.21
	12-15‡	No data (2082)	2390 (2183)	1210 (1490)	No data	99.02	99.20
	12-16‡	1930 (2590)	2390 (2576)	1780 (1485)	98.54	98.94	98.99
SO_3 (Expressed as SO_4)	12-14	No data	12.9	3.0	No data	0.37	1.77
	12-15‡	No data	29.4	9.25	No data	0.81	0.51
	12-16‡	34.3	36.6	20.5	1.17	1.01	0.76
Particulate Sulfate (as SO_4)	12-14	No data	5.33	5.14	No data	0.15	3.02
	12-15‡	No data	5.81	5.3	No data	0.16	0.29
	12-16‡	8.57	1.7	6.69	0.29	0.046	0.25
Total Primary Sulfate	12-14	No data	18.2	8.14	No data	0.52	4.79
	12-15‡	No data	35.2	14.6	No data	0.98	0.80
	12-16‡	42.8	38.3	27.2	1.46	1.06	1.01

*Level 2.

†Data in parentheses are from simultaneous continuous monitoring.

‡FGD system operated in acid cleaning mode on these days.

the scrubber outlet show the same increasing trend as at the scrubber inlet. For the 12-14 test, an average of 77% of the SO_3 was removed by scrubbing. Emitted SO_3 comprised 1.8% of the total sulfur species present in the flue gas when the FGD unit was in normal operation.

Particulate Sulfate--

Particulate sulfate data are available from three independent measurement methods: CCS, SASS train, and MRI impactor. These data are presented in Tables 15, 16, and 17, respectively. SASS and CCS data are available at the ESP inlet. Particulate sulfate measured by the SASS was 21.8 ng/J, compared to 8.57 ng/J measured with the CCS. The CCS measurement seems low, compared to an average uncontrolled particulate sulfate emission factor of 28 ng/J based on fuel sulfur and data from Reference 4. This figure is also greater than the SASS emission factor. However, as previously stated, ESP inlet particulate measurements with the SASS are suspected of being low. Therefore, the CCS data for particulate sulfate at the ESP inlet is considered very low. This could be due to load differences (265 MW for the SASS vs. only 191 MW for the CCS). Another explanation involves sampling point geometry, i.e., the CCS probe is short and samples flue gas perpendicular to the flow, whereas the SASS probe is a nozzle centered in the duct and pointed into the flow.

Data for particulate sulfate from all three trains are available at the ESP outlet. These data show emission factors of 0.923 ng/J with the SASS, 1.75 and 0.44 ng/J with the MRI impactor, and 5.33, 5.81, and 1.7 ng/J with the CCS. Excluding the two highest CCS values, average ESP-controlled particulate sulfate emissions of 1.2 ng/J at Cane Run agree reasonably well with an emission factor of 1.13 ng/J calculated from fuel sulfur and data on ESP-controlled emissions from dry bottom bituminous coal-fired utility boilers from Reference 4. However, a review of boiler and CCS sampling train operating conditions reveals no apparent reason for the two CCS data points having a high bias. Combining all data points into a mean ESP-controlled emission factor for Cane Run, a value of 2.66 ng/J is obtained (standard deviation, 2.31 ng/J). Both the Cane Run data and the data base for Reference 4 show high variability, so there seems no reason to eliminate

TABLE 16. PARTICULATE SULFATE EMISSIONS AS DETERMINED FROM SASS PARTICULATE CATCH*

Aerodynamic Diameter Size Range, μm	Particulate Sulfate Emissions, ng/J		
	ESP Inlet	ESP Outlet	Scrubber Outlet
>10	3.75		
	9.75	0.0528	0.590
3 - 10	6.00		
1 - 3	5.64		
	12.03	0.870	1.99
<1	6.39		
Total	21.8	0.923	2.58

* The SASS is a Level 1 sampling method. Sulfate was determined by Level 2 procedures

any of the data from Cane Run as outliers. Considerable data scatter is likely due to coal variability; the extent of this, however, is unknown.

Emissions of particulate sulfate after scrubbing were measured with all three trains. Measured emission factors were 2.58 ng/J with the SASS, 3.08 and 6.31 ng/J with the MRI impactor, and 5.14, 5.3, and 6.69 ng/J with the CCS. The three highest values were measured during FGD operation in acid cleaning mode, indicating that some increase in particulate emissions may be due to acid cleaning. However, outlet sulfate particulate loadings seem to be consistently equal to or greater than inlet loadings at the scrubber. The average of all outlet loading data is 4.85 ng/J (standard deviation, 1.68 ng/J). Excluding data obtained on acid cleaning days, the mean is 3.60 ng/J (standard deviation, 1.36 ng/J).

Particulate sulfate size distribution data from SASS and MRI tests show that sulfate mass emissions of small particles are greater than for large particles. MRI sulfate data, which include some very small H_2SO_4 aerosol droplets in the particulate catch, show a major fraction of the particulate sulfate emitted to the atmosphere is less than 0.5 μm in diameter.

TABLE 17. PARTICULATE SULFATE EMISSIONS DETERMINED FROM MRI PARTICULATE

Test Date	Stage	Scrubber Inlet			Scrubber Outlet		
		D_{50}, µm	Concentration mg/m3	Emission Factor, ng/J	D_{50} µm	Concentration mg/m3	Emission Factor, ng/J
12-13	1	28.64	3.4	1.4	23.43	Blank	---
	2	14.04	0.01	0.004	11.48	Blank	---
	3	5.256	0.15	0.060	4.284	0.26	0.13
	4	2.389	0.23	0.091	1.937	0.43	0.22
	5	1.368	0.08	0.03	1.101	0.33	0.17
	6	0.6426	<Blank	---	0.5083	0.51	0.26
	7	0.4241	No Plate	---	0.3298	No Plate	---
	Filter	---	0.54	0.21	---	4.44	2.29
	Total	---	4.41	1.75	---	5.97	3.08
12-14	1	31.65	No Plate	---	24.10	0.04	0.02
	2	15.52	<Blank	---	11.81	0.04	0.02
	3	5.819	0.10	0.040	4.407	0.43	0.19
	4	2.652	0.29	0.12	1.994	1.72	0.772
	5	1.523	0.22	0.088	1.134	0.68	0.31
	6	0.7214	0.004	0.002	0.5238	1.15	0.516
	7	0.4800	0.04	0.02	0.3401	No Plate	---
	Filter	---	0.45	0.18	---	10.0	4.49
	Total	---	1.10	0.44	---	14.06	6.31

Total Primary Sulfate--

Primary sulfates are composed of two components: gaseous SO_3 and particulate sulfate. The proportion of each component changes with flue gas temperature and moisture content. Thus, the exact composition of the sulfate mixture can be different from point to point in the combustion process, and may change further when the flue gas is emitted to the atmosphere. Therefore, it is best to focus on the total quantity and nature of primary sulfate emissions, rather than on SO_3 or particulate sulfate individually. The effectiveness of control devices in reducing total primary sulfate emissions is a key factor in evaluating emission control system performance.

A best estimate of total primary sulfate emissions was made using the combined data from SASS, CCS, and MRI impactor runs. At the ESP inlet, total primary sulfates were 56.1 ng/J, composed of 34.3 ng/J of SO_3 (CCS) and 21.8 ng/J of particulate sulfate. This value is probably a reasonable estimate. The SASS particulate data point is probably low due to particulate stratification, but the SO_3 data point is probably high due to low load and high oxygen concentrations. The two effects tend to cancel each other. At the ESP outlet, the three-day average of CCS SO_3 data is 26.3 ng/J and the average of all test data for particulate sulfate is 2.66 ng/J, giving a total primary sulfate emission factor of 29.0 ng/J. Only data taken during normal FGD operation were used to compute the emission factor at the scrubber outlet. Emissions of SO_3 were 3.0 ng/J (CCS) and particulate sulfate emissions were 3.60 ng/J (average of SASS data, 12-13 MRI data, and 12-14 CCS data), giving a total primary sulfate emission factor of 6.6 ng/J at the scrubber outlet. Total primary sulfate removal efficiencies based on these data were 48% across the ESP and 77% across the scrubber, for an overall removal of 88%.

The nature, as well as the quantity, of emitted primary sulfates can be determined from the Cane Run data. The net increase in particulate sulfate across the scrubber is probably due to conversion of incoming SO_3 to aerosol H_2SO_4 droplets and entrainment of scrubber liquor in the gas stream. The amount of this increase can be estimated as follows. Assuming the inlet particulate matter contains negligible H_2SO_4 aerosol because of the high temperature, all the particulate sulfate is metallic sulfate. If it is

assumed these sulfates are removed to the same extent as total particulates, the amount of particulate sulfate at the outlet exclusive of H_2SO_4 aerosol and entrained scrubber liquor can be estimated. Using 9.20 ng/J and 7.46 ng/J for inlet and outlet total particulate loadings and 2.66 ng/J inlet particulate sulfate, outlet metallic sulfates should amount to 2.16 ng/J. Thus, H_2SO_4 aerosol and entrained scrubber liquor amount to 3.60 - 2.16 or 1.44 ng/J. FTIR data from Appendix D indicate that about 0.48 ng/J can be attributed to sulfate from the scrubber solution. The balance, 0.96 ng/J, is due to conversion of SO_3 to H_2SO_4 aerosol in the scrubber. In summary, about 48% of the total particulate emitted is sulfate, of which 60% is metallic sulfate from coal ash, 30% is sulfate as H_2SO_4 aerosol droplets (or adsorbed sulfate), and 10% is sulfate from the scrubber liquor. Furthermore, most of the emitted sulfate particles are less than 0.5 μm in diameter and are thus readily inhaled.

4.4.4 Inorganics

Major and trace elements in the flue gas were primarily determined by inductively coupled plasma optical emission spectroscopy (ICP). Trace elements not determined by ICP are arsenic and antimony which were determined by atomic absorption and mercury which was determined by a cold vapor method. Concentrations of 25 elements present in the flue gas are presented in Tables 18 and 19. To assess the hazard potential of these elemental concentrations, the data are compared with the Discharge Multimedia Environmental Goal (DMEG) values for these elements. The DMEG values are emission level goals developed under the direction of EPA, and can be considered as concentrations of pollutants in undiluted emission streams that will not adversely affect those persons or ecological systems exposed for short periods of time (5). The DMEG values tabulated represent air concentrations which were derived from human health considerations based upon the most hazardous compound formed by the element in question. Additionally, estimated ambient concentrations, based upon measured emission concentrations, are compared with the Ambient Multimedia Environmental Goal (AMEG) values. Tabulated AMEG values are analogous to DMEG values with the exception that AMEG concentrations will not adversely affect persons or ecological systems subjected to continuous exposure.

TABLE 18. FLUE GAS CONCENTRATIONS OF MAJOR AND TRACE ELEMENTS

Element	Concentration, mg/dscm		DMEG for Air (Health Basis)	Discharge Severity	
	ESP Inlet (6.64% O_2)	ESP Outlet (7.06% O_2)	mg/m^3	ESP Inlet	ESP Outlet
Al	640	1.67	5.2	120	0.32
As	1.49	0.0100	0.0020	745	5.0
B	12.7	8.12	3.1	4.1	2.6
Ba	1.00-1.02	0.0049 -0.0200	0.50	2.0	0.0098-0.040
Ca	49.0	0.456	16	3.1	0.029
Cd	0.012-0.0155	<0.0041	0.010	1.2-1.6	0-0.41
Co	0.224-0.229	0.0172	0.050	4.5-4.6	0.34
Cr	0.265	0.0033	0.0010	265	3.3
Cu	0.591	0.0360	0.20	3.0	0.18
Fe	802	1.98	1.0	802	2.0
Hg	0.00042	0.00070	0.050	0.0084	0.014
K	69.7	0.177-0.226	2.0	35	0.089-0.11
La	0.208-0.210	<0.0021	110	0.0019	<0.00002
Li	0.325	0.0049	0.022	15	0.22
Mg	47.1	0.127	6.0	7.9	0.021
Mn	1.29	0.0726	5.0	0.26	0.015
Na	3.75-3.80	0.328-0.377	53	0.071	0.0062-0.0071
Ni	0.470	0.00070-0.00011	0.015	31	0.047-0.073
P	4.94-4.96	0.030-0.046	0.10	49-50	0.30-0.46
Pb	0.787	<0.0009	0.15	5.2	<0.006
Sb	<0.006	<0.005	0.50	<0.01	<0.01
Si	1.40	0.233	10	0.14	0.023
Sr	0.719-0.754	0.075-0.076	3.0	0.24-0.25	0.025
V	1.36	0.0088	0.50	2.7	0.018
Zn	1.16	0.015	4.0	0.29	0.0039

TABLE 19. CONCENTRATIONS OF MAJOR AND TRACE ELEMENTS IN STACK EMISSIONS

Element	Concentration µg/dscm (8.26% O_2)	DMEG, µg/m^3 (Health Basis)	Discharge Severity	AMEG, µg/m^3 (Health Basis)	Ambient Severity*
Al	961	5,200	0.18	12.6	0.153
As	14.3	2.0	7.2	0.0050	5.8
B	252	3,100	0.081	74	0.0068
Ba	<17	500	<0.034	1	<0.034
Ca	275	16,000	0.017	No data†	---
Cd	<4	10	<0.4	0.02	<0.4
Co	1.8 -1.9	50	0.036-0.038	0.1	0.04
Cr	16.6	1	17	0.002	17
Cu	14	200	0.068	0.5	0.054
Fe	1,960	1,000	2.0	No data	---
Hg	0.017	50	0.00034	0.01	0.0034
K	98-150	2,000	0.049-0.077	5	0.04-0.06
La	<2	110,000	<0.00002	No data	---
Li	0.28-0.48	22	0.013-0.022	0.05	0.011-0.019
Mg	62.2	6,000	0.010	14	0.0088
Mn	26	5,000	0.0052	12	0.0044
Na	495-551	53,000	0.0093-0.010	No data	---
Ni	11.6-11.9	15	0.77-0.79	0.035	0.66-0.68
P	13-32	100	0.13-0.32	0.24	0.11-0.26
Pb	<1	150	<0.007	0.36	<0.006
Sb	<6	500	<0.01	1.2	<0.01
Si	<6	10,000	<0.0006	No data	---
Sr	57.8-59.2	3,000	0.019-0.020	5.5	0.022
V	5.45	500	0.01	1.2	0.009
Zn	44.5	4,000	0.011	9.5	0.009

*Ambient discharge severity is defined as the ratio of the ambient concentration to the AMEG value. Ambient concentration is estimated to be the ratio of discharge concentration to a dilution factor based on flue gas flow rate. Flue gas flow rate averaged 3.47 x 10^5 g/s during SASS Level 1 tests, corresponding to a dilution factor of 500.

†No AMEG value has been established for these elements.

Elemental concentrations were determined by analyzing the SASS catches obtained during the test period. As will be discussed in the Appendices, major and trace elements are recovered from the particulate catches by aqua regia extraction. Because some particulate constituents are insoluble in aqua regia (i.e., silica and some aluminosilicates), tabulated elemental concentrations do not necessarily reflect the total elemental concentration in the flue gas. However, the rigorous extraction procedure employed ensures that tabulated elemental concentrations are equal to or greater than concentrations available to the environment as a result of natural extraction processes.

Elemental data presented in Table 18 indicate that at least 17 elements exceeded their respective DMEG values at the ESP inlet (Al, As, B, Ba, Ca, Cd, Co, Cr, Fe, K. Li, Mg, Ni, P, Pb, and V). Because the SASS particulate catch at the ESP inlet appears to have been low as a result of particulate stratification, other elements may also have exceeded their DMEG values at this location. ESP outlet data indicate that, after particulate removal by the ESP, only four elements exceeded their respective DMEG values. These four elements - arsenic, boron, chromium, and iron - would be of concern in the absence of further flue gas treatment. The DMEG value for arsenic is low because arsenic is a cumulative poison producing chronic effects in humans. Chromium has a low DMEG value due to considerations of potential human carcinogenicity.

Scrubber outlet data presented in Table 19 show that As, Cr, and Fe exceed their respective DMEG values. The concentrations of As and Cr exceed their respective AMEG values. Thus, arsenic and chromium may present a health hazard from both short term direct exposure and long term continuous exposure after dispersion.

Major and trace element emission factors are presented in Table 20. The overall elemental removal efficiency of the ESP was measured to be 99.2%; however, the actual removal efficiency may have been higher since concentrations at the ESP inlet are lower limit values as a result of particulate stratification. The overall elemental removal efficiency of the scrubber was 63 to 65%, resulting in an average combined removal efficiency exceeding 99.7%.

TABLE 20. EMISSION FACTORS FOR MAJOR AND TRACE ELEMENTS

Element	Emission Factor, pg/J			Removal Efficiency, Percent		
	ESP Inlet	ESP Outlet	Scrubber Outlet	ESP	Scrubber	Overall
Al	253,000	678	433	99.73	36.2	99.83
As	588	4.05	6.43	99.31	NM	98.9
B	5,010	3,300	113	34.2	96.6	97.7
Ba	395-401	2.0-8.1	<7.7	97.9-99.50	Unknown	>98.1
Ca	19,300	166	124	99.14	25.4	99.36
Cd	4.5-6.1	<2	<2	>63	Unknown	>60
Co	88-90	7.0	0.81-0.85	92.1	88	99.0-99.1
Cr	105	1.34	7.47	98.7	NM	92.9
Cu	233	14.6	6.1	93.7	58	97.4
Fe	316,000	803	883	99.75	NM	99.72
Hg	0.165	0.285	0.008	NM	97	95
K	27,500	72-92	44-69	99.67-99.74	3.5-52	99.75-99.84
La	82-83	<0.8	<0.9	99.0	Unknown	>99
Li	128	2.0	0.13-0.22	98.4	89-94	99.8-99.9
Mg	18,600	51.5	28.0	99.72	45.6	99.85
Mn	509-553	29.5	12	94.2-94.7	60	97.7-97.8
Na	1,480-1,500	133-153	223-248	89.6-91.1	NM	83.2-85.1
Ni	185	0.3-0.4	5.22-5.36	99.8	NM	97
P	1,950	12.1-18.6	5.8-14	99.0-99.4	<69	99.3-99.7
Pb	311	<0.4	<0.3	>99.9	Unknown	>99.9
Sb	<2	<2	<3	Unknown	Unknown	Unknown
Si	553	94.7	<3	82.9	>97	>99.5
Sr	284-297	30-31	26-27	89-90	13-16	91
V	535	3.56	2.45	99.33	31.2	99.54
Zn	458	6.3	20.0	98.6	NM	95.6

Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) studies were performed on particulate samples to identify specific inorganic compounds. In general, XRD results were inconclusive, except to identify silicate minerals in flue gas particulate. Detailed FTIR results and spectra are presented in Appendix D. FTIR analysis clearly showed that $CaSO_4$ and $NaHSO_4$ tended to be found in the smaller (<1 μm) particle sizes. FTIR positively identified calcium sulfate in the scrubber outlet. None had been clearly detected in the inlet, though weak evidence from XRD studies suggest some $CaSO_4$ may have been present. An unidentified sulfate was detected at the scrubber outlet using FTIR. Elemental data and FTIR results indicate this may have been an oxidation product of $NaHSO_3$ emitted with entrained scrubber liquor. The sulfate was estimated to be present at less than 0.5 ng/J, and to constitute less than 10% by weight of total particulate emissions.

Flue gas nitrate data were obtained by extraction of SASS catches and are summarized in Table 21. Separate nitrate determinations were made for the >3 μm particulate fractions and the <3 μm particulate fractions. These data indicate nitrate levels of 0.0126 to 0.0359 ng/J at the ESP inlet, 0.0016 ng/J at the ESP outlet, and 0.0018 ng/J at the scrubber outlet.

TABLE 21. FLUE GAS NITRATE EMISSION FACTORS

Aerodynamic Diameter Size Range, μm	Emission Factor, ng/J		
	ESP Inlet	ESP Outlet	Scrubber Outlet
>3	0.0233	Not Analyzed	Not Analyzed
<3	0.0126	0.0016	0.0018*
Total	0.0126 - 0.0359	0.0016	0.0018*

*Only the particulate filter catch was analyzed. Insufficient sample of the 1 μm cyclone catch was available for analysis. Therefore, value may be low.

Specific anion analyses were also performed on the extracts from particulate catches and impinger solutions from the CCS. Chloride and fluoride analyses are summarized in Table 22. Emissions of particulate chloride and HCl at the scrubber outlet averaged 0.087 and 0.089 ng/J, respectively. Chloride concentrations at the scrubber outlet equate to a discharge severity of 0.47, based on a DMEG value of 7000 $\mu g/m^3$. The removal efficiency of particulate chloride by the ESP cannot be reliably computed since particulate catches at the ESP inlet are low as a result of particulate stratification. A slight increase in average particulate chloride emissions was noted across the scrubber. HCl was not removed by the ESP, although scrubbing effected at least 95% removal.

Emissions of particulate fluoride and HF at the scrubber outlet were variable, but the total fluoride emission was fairly constant, averaging 0.12 ng/J. Fluoride concentrations at the ESP inlet and outlet exceeded the DMEG value (2.5 $\mu g/m^3$) but the discharge severity at the scrubber outlet averaged 0.096. No good estimate of particulate fluoride removal by the ESP or scrubber can be made from the data. Little or no HF was removed by the ESP, although scrubbing effected approximately 98% removal.

These data indicate that neither Cl^- or F^- emissions appear to pose a health hazard with short term direct exposure. AMEG values have not been established for these anions, so the potential hazards of long term exposure after dispersion cannot be evaluated.

4.4.5 Organic Emissions

Flue gas samples at the ESP inlet, ESP outlet, and scrubber outlet obtained during Level 1 testing were analyzed for specific organic compounds and compound types. Organics in the C_1-C_6 range were measured by gas chromatographic (GC) analysis of bag samples. SASS samples were analyzed by gas chromatograph to determine C_7-C_{16} organics and by gravimetric analysis to determine higher molecular weight ($>C_{16}$) organics. Analyses for C_7-C_{16} and $>C_{16}$ were also performed on seven liquid chromatograph (LC) fractions of each SASS sample. Infrared analyses were performed to identify compound classes, and gas chromatography/mass spectrometry (GC/MS) was used to quantitate specific compounds of polycyclic organic matter (POM).

TABLE 22. CHLORIDE AND FLUORIDE EMISSIONS DETERMINED WITH THE CONTROLLED CONDENSATION SYSTEM*

Compound	Test Date	Emission Factor, ng/J			Removal Efficiency Percent	
		ESP Inlet	ESP Outlet	Scrubber Outlet	Scrubber	Overall
Particulate	12-14	No data	0.036	0.094	NM†	Unknown
Chloride	12-15	No data	0.083	0.087	NM	Unknown
(as Cl^-)	12-16	0.084	0.090	0.079	12.82	5.87
HCl	12-14	No data	3.3	0.03	99.00	Unknown
	12-15	No data	2.2	0.066	97.00	Unknown
	12-16	2.8	3.23	0.17	94.78	93.89
Particulate	12-14	No data	0.099	0.13	NM	Unknown
Fluoride	12-15	No data	<Blank	0.066	Unknown	Unknown
(as F^-)	12-16	0.058	<Blank	<Blank	Unknown	Unknown
HF	12-14	No data	2.9	0.01	99.52	Unknown
	12-15	No data	2.8	0.04	98.42	Unknown
	12-16	4.2	4.3	0.12	97.27	97.18

* Level 2.

† Not Meaningful.

Results of the GC analyses for C_1-C_6 organics are presented in Table 23. The majority of C_1-C_6 organics are present in the C_1 and C_2 fractions. The emission factor for C_1-C_6 organics at the scrubber outlet ranges from 1.2 to 3.1 ng/J. Increases across the scrubber are probably due to organic emissions from the oil-fired reheaters in the FGD system.

Chromatographic and gravimetric analyses of SASS samples are summarized in Table 24. Most C_7-C_{16} organics measured at the ESP inlet and outlet were present in the C_8 and C_9 fractions. Other fractions were present at levels which were orders of magnitude lower. At the scrubber outlet, the highest concentrations of C_7-C_{16} organics were present in the C_{12}-C_{16} fractions. Total chromatographable organics (TCO) measured 0.072 ng/J at the ESP inlet, 0.42 ng/J at the ESP outlet, and 0.366 ng/J at the scrubber outlet.

Higher molecular weight organics (>C_{16}) totalled 0.30 ng/J at the ESP inlet, 0.12 ng/J at the ESP outlet, and 1.46 ng/J at the scrubber outlet. Not all of the >C_{16} organics were recovered from the XAD-2 resin. In the ESP inlet sample, 13% of the total catch was found in the probe rinse and 10 μm and 3 μm cyclones, and another 12% in the 1 μm cyclone and particulate filter catches. At the ESP outlet and scrubber outlet, the probe rinse accounted

TABLE 23. C_1-C_6 ORGANICS IN THE FLUE GAS*

Sampling Location	Date	Emission Factor, ng/J						
		C_1	C_2	C_3	C_4	C_5	C_6	Total
ESP Inlet	12-7	0.50	<0.05	<0.08	<0.1	<0.1	<0.2	0.5 -1.0
ESP Outlet	12-6	0.18	0.41	<0.08	<0.1	<0.1	<0.2	0.59-1.1
	12-7	1.11	0.86	<0.08	<0.1	<0.1	<0.2	2.0 -2.5
Scrubber Outlet	12-6	0.94	0.21	<0.09	<0.1	<0.1	<0.2	1.2 -1.7
	12-7	1.11	1.50	<0.09	<0.1	<0.1	<0.2	2.6 -3.1

*Level 1 analysis by gas chromatography. Totals may not equal sum of C_1-C_6 due to rounding error.

TABLE 24. ORGANICS GREATER THAN C_6 IN FLUE GAS*

Organic	Emission Factor, ng/J		
	ESP Inlet	ESP Outlet	Scrubber Outlet
C_7	<0.0004	<0.0004	0.002
C_8	0.0517	0.4077	0.0016
C_9	0.015	0.0081	0.0045
C_{10}	0.001	<0.0004	0.027
C_{11}	<0.0004	<0.0004	0.021
C_{12}	0.001	0.0008	0.059
C_{13}	0.001	0.0008	0.039
C_{14}	0.0008	<0.0004	0.0617
C_{15}	0.0008	0.0004	0.0837
C_{16}	0.0004	0.0004	0.0531
Total TCO	0.072	0.42	0.366
Total Grav (>C_{16})†	0.30	0.12	1.46
TCO + Grav	0.37	0.54	1.82

*Total chromatographable organics (TCO), $C_7 - C_{16}$, were determined by gas chromatography (Level 1). The >C_{16} fraction (Grav) was determined gravimetrically (Level 1).

†Contributions to the >C_{16} fraction from SASS train components other than the XAD-2 resin were not negligible. See text.

for 9% and 1% of the total $>C_{16}$ organics, respectively. None of the cyclone or filter catches were used for LC. The large increase in $>C_{16}$ organics across the scrubber is probably due to formation of POM in the oil reheaters. This conclusion is verified by POM data which are discussed separately. IR analyses of sample concentrates are detailed in Appendix C.

Because the concentrations of C_7-C_{16} and $>C_{16}$ organics exceeded 0.5 mg/m^3 at all sampling points, the SASS samples were fractionated by LC separation. LC separation results are presented in Tables 25, 26, and 27. Almost all the TCO in ESP inlet and outlet samples resided in the LC4-LC6 fractions, while at the scrubber outlet, TCO in the LC1 fraction predominated. IR analyses of LC fractions are detailed in Appendix C.

Table 28 presents POM emission data. Total POM at the ESP inlet ranged from 4.2 to 14.2 $\mu g/m^3$ and from 8.6 to 10.0 $\mu g/m^3$ at the ESP outlet. Naphthalene was the compound present at the highest concentrations at both locations. Nonetheless, the concentration of naphthalene was at least four orders of magnitude less than its DMEG value of 50 mg/m^3. The total POM concentration of 160 $\mu g/m^3$ at the scrubber outlet is an order of magnitude greater than at the scrubber inlet. Seventeen compounds were present above the detection limit of approximately 0.3 $\mu g/m^3$. Phenanthrene was present at the highest concentration (37 $\mu g/m^3$) and had the highest discharge severity (0.023). The increased POM emissions are probably due to poor combustion in the oil-fired reheaters.

4.5 LIQUID WASTES AND PROCESS LIQUIDS

Five liquid streams were sampled in the field. These streams included make-up water (from the Ohio River), ash pond overflow, sump #6 discharge, carbide lime liquid, and bottom ash liquid. Two of the five streams, the ash pond overflow and sump #6 liquid, are discharged into the Ohio River. The other three streams are either input streams (make-up water, carbide lime liquid) or process streams (bottom ash liquid). The ash pond overflow comes from a pond receiving liquid effluents from two other units as well as Cane Run No. 6. Samples were obtained by tap sampling, except for bottom ash slurry and ash pond overflow, which were grab sample. All samples for chemical analysis were obtained on 12-14.

TABLE 25. LC ANALYSIS OF FLUE GAS AT THE ESP INLET
(SAMPLE: 167-XMCD-SE-KD)

	TCO mg	Grav mg	TCO + Grav mg	Concentration mg/DSCM
Total Sample*	5.54	17.33	22.87	0.755
Taken for LC†	3.88	12.11	15.99	0.528
Recovered‡	1.17	2.27	3.44	0.114

	TCO in mg				Grav in mg					
Fraction	Found in Fraction	Blank	Corrected	Total**	Found in Fraction	Blank	Corrected	Total**	TCO + Grav Total mg	Concentration mg/DSCM
LC1	0.18	0.34	0.00	0.00	1.58	0.07	1.51	2.16	2.16	0.071
LC2	0.00	0.02	0.00	0.00	0.32	0.05	0.24	0.34	0.34	0.011
LC3	0.06	0.00	0.06	0.09	0.41	0.14	0.27	0.39	0.48	0.016
LC4	0.38	0.04	0.34	0.49	0.31	0.17	0.14	0.20	0.69	0.023
LC5	0.44	0.01	0.43	0.61	0.19	0.08	0.11	0.16	0.76	0.025
LC6	0.43	0.09	0.34	0.49	1.44	2.27	0.00	0.00	0.49	0.016
LC7	0.00	0.00	0.00	0.00	0.89	5.08	0.00	0.00	0.00	0.000
Totals			1.17	1.68			2.27	3.25	4.92	0.162

* The 167-XMCD-SE-KD sample represented 80% of the TCO + Grav total reported for Site 167 and was the sample used for LC; values reported are for quantity in entire 167-XMCD sample before LC.

† Portion of whole sample used for LC, actual mg.

‡ Quantity recovered from LC column, actual mg.

** Total mg computed back to total sample.

TABLE 26. LC ANALYSIS OF FLUE GAS AT THE ESP OUTLET
(SAMPLE: 168-XMCD-SE-KD)

	TCO mg	Grav mg	TCO + Grav mg	Concentration mg/DSCM
Total Sample*	63.0	16.9	79.9	1.305
Taken for LC†	39.1	10.5	49.6	0.810
Recovered‡	19.9	7.0	26.9	0.440

	TCO in mg				Grav in mg					
Fraction	Found in Fraction	Blank	Corrected	Total**	Found in Fraction	Blank	Corrected	Total**	TCO + Grav Total mg	Concentration mg/DSCM
LC1	0.67	0.62	0.05	0.08	0.72	0.13	0.59	0.95	1.03	0.017
LC2	0.23	0.04	0.19	0.31	0.40	0.15	0.25	0.40	0.71	0.012
LC3	0.07	0.00	0.07	0.11	0.80	0.25	0.55	0.89	1.00	0.016
LC4	1.73	0.07	1.66	2.67	1.24	0.31	0.93	1.50	4.17	0.068
LC5	11.80	0.02	11.78	18.97	0.67	0.15	0.52	0.84	19.81	0.324
LC6	6.28	0.16	6.12	9.86	8.27	4.13	4.14	6.67	16.53	0.270
LC7	0.00	0.00	0.00	0.00	2.15	9.25	0.00	0.00	0.00	0.000
Totals			19.87	32.00			6.98	11.24	43.25	0.707

* Quantity in entire sample, determined before LC.

† Portion of whole sample used for LC, actual mg.

‡ Quantity recovered from LC column, actual mg.

** Total mg computed back to total sample.

TABLE 27. LC ANALYSIS OF FLUE GAS AT THE SCRUBBER OUTLET
(SAMPLE: 169-XMCD-SE-KD)

	TCO mg	Grav mg	TCO + Grav mg	Concentration mg/DSCM
Total Sample*	43.51	171.4	214.9	4.011
Taken for LC†	28.06	110.6	138.6	2.587
Recovered‡	28.44	123.25**	151.69	2.831

Fraction	TCO in mg				Grav in mg				TCO + Grav Total mg	Concentration mg/DSCM
	Found in Fraction	Blank	Corrected	Total††	Found in Fraction	Blank	Corrected	Total††		
LC1	23.70	0.68	23.02	35.70	71.14	0.14	71.00	110.08	145.78	2.72
LC2	1.14	0.04	1.10	1.71	9.47	0.16	9.31	14.43	16.14	0.30
LC3	1.96	0.00	1.96	3.04	12.80	0.28	12.52	19.41	22.45	0.42
LC4	1.24	0.08	1.16	1.80	6.07	0.34	5.73	8.88	10.68	0.20
LC5	0.44	0.02	0.42	0.65	3.85	0.16	3.69	5.72	6.37	0.12
LC6	0.46	0.18	0.28	0.43	25.54	4.54	21.00	32.56	32.99	0.62
LC7	0.00	0.00	0.00	0.00	2.60	10.16	0.00	0.00	0.00	0.00
Totals			28.44	43.33			123.25	191.08	234.41	4.38

* Quantity in entire sample, determined before LC.

† Portion of whole sample used for LC, actual mg.

‡ Quantity recovered from LC column, actual mg.

** Sample taken for LC was too large for efficient desiccation as seen by high Grav recovery; after two weeks' desiccation, residues were redissolved for IR and LRMS analysis.

†† Total mg computed back to total sample.

TABLE 28. FLUE GAS POM ANALYSES

Sample	POM Compound	Concentration, $\mu g/m^3$
ESP Inlet (6.64% O_2)		
167-PR-CC	Naphthalene	T*(<3)
	Dimethylnaphthalene	T (<3)
167-XMCD	Naphthalene	4.2
	Phenanthrene	T (<2)
	Methylphenanthrene	T (<2)
167-FC	No POM detected	<0.03
167 (Total)	Total POM	4.2 - 14.2
ESP Outlet (6.06% O_2)		
168-PR	Naphthalene	T (<1)
168-XMCD	Naphthalene	7.6
	Biphenyl	1
	Phenanthrene	T (<0.2)
	Methylphenanthrene	T (<0.2)
168 (Total)	Total POM	8.6 - 10.0
Stack (8.26% O_2)		
169-PR	Naphthalene	T (<1)
169-XMCD	Naphthalene	27
	Biphenyl	14
	Acenaphthene	T (<1)
	2,6-Dimethylnaphthalene	3.0
	1,3-Dimethylnaphthalene	13
	1,7-Dimethylnaphthalene	24
	2,3-Dimethylnaphthalene	12
	Fluorene	6
	Phenanthrene	37
	Methylfluorene	2.5
	Dibenzothiophene	3.0
	Methylphenanthrene	5.1
	Methylphenanthrene	4.6
	Fluoranthene	1
	Pyrene	5.5
	1,2-Benzofluorene	T (<1)
	Chrysene	T (<1)
169 (Total)	Total POM	160

*T = trace; compound present above detection limit of about 0.3 $\mu g/m^3$ but below level required for accurate quantitation.

Samples from all five streams were analyzed in the field for standard water quality parameters using Level 1 procedures. In addition, all samples were analyzed in the laboratory for inorganics using Level 2 methodology. With the exception of the carbide lime liquid stream, laboratory analyses were also performed on the liquid samples to determine concentrations of organics. Results of analysis have, where possible, been compared to those levels thought to be safe in terms of ecological and health considerations.

4.5.1 Water Quality Parameters

Characteristics of the five liquid streams are listed in Table 29. The concentration of cyanide in the carbide lime liquid stream was much higher than in the other four streams. This may be due to the acetylene process by which the carbide lime is made. Cyanide is a by-product of this process. Phosphate concentration was high in the ash pond overflow, possibly due to the high phosphorus concentration in the coal. Unusually high sulfite and sulfate concentrations, and high alkalinity, in the ash pond overflow are likely due to the fact that the other two units using the ash pond have lime scrubbers which discharge into the pond.

4.5.2 Inorganic Analyses

Inorganic analysis results for the five liquid streams are presented in Table 30. The appropriate health and ecological DMEG values are also listed, and discharge severities have been calculated. It should be noted that only sump #6 discharge (about 5.4 m^3/hr) and ash pond overflow are actually discharged to surface waters.

Only a few measured values exceed, or potentially exceed, the DMEG health values in liquid streams. In all cases, the streams are either the make-up water, the sump #6 discharge, or the carbide lime liquid. The ash pond overflow, which is discharged to the river, exceeds no DMEG health values. The sump #6 discharge poses potential health problems with iron and manganese. However, it is important to note that concentrations of these two elements, relatively common pollutants in natural waters, are discharged in lower concentrations than are present in the incoming make-up water.

TABLE 29. WATER QUALITY PARAMETERS*

Liquid Stream	Temperature °C	pH†	Hardness (as $CaCO_3$) mg/l	Alkalinity (as $CaCO_3$) mg/l	Nitrate mg/l	Ammonia Nitrogen mg/l	Cyanide mg/l	Phosphate Phosphorus mg/l	Sulfite ($SO_3^=$) mg/l	Sulfate ($SO_4^=$) mg/l	$SO_4^=$ (lab) mg/l‡
Make-up Water	13**	7.80 ± 0.21	No data	No data	1.5	0.3	<0.01	0.65	85	90	54
Ash Pond Overflow	8.5	8.89 ± 0.15	120	60	0.5	<0.01	<0.01	2.8	500	600	471
Sump No. 6 Discharge	21**	8.89 ± 0.12	80	80	2.0	3.2	<0.01	0.95	90	90	103
Carbide Lime Liquid	11	12.67 ± 0.15	250	1600	0.8	2.1	1.2	<0.05	0.5	8	34
Bottom Ash Slurry	11.5	9.53**	40	60	1.0	0.35	<0.01	0.35	150	150	72

* Level 1 procedures were utilized.

† pH was measured on each of three days; 12-6, 12-7, 12-14. Indicated values are mean of three readings ± one standard deviation, unless otherwise indicated.

‡ This is a laboratory measurement. All others were performed in the field.

** Average of two measurements.

TABLE 30. MAJOR AND TRACE ELEMENT CONCENTRATIONS IN LIQUID STREAMS*

Element	DMEG, mg/l		Make-Up Water			Ash Pond Overflow		
	Health	Ecology	mg/l	Discharge Severity		mg/l	Discharge Severity	
				Health	Ecology		Health	Ecology
Al	80	1.0	0.83	0.01	0.83	0.42	0.005	0.42
As	0.25	0.05	0.06	0.24	1.2	<0.02	<0.08	<0.4
B	47	25	<0.005	<0.0001	<0.0002	3.46	0.074	0.138
Ba	5.0	2.5	<0.03	<0.006	<0.01	<0.03	<0.006	<0.012
Ca	240	16	43.1	0.18	2.7	110	0.458	6.9
Cd	0.050	0.001	<0.007	<0.14	<7.0	<0.007	<0.14	<7.0
Co	0.75	0.25	0.015	0.02	0.06	<0.009	<0.012	<0.036
Cr	0.25	0.25	<0.01	<0.04	<0.04	<0.01	<0.04	<0.04
Cu	5.0	0.050	0.010	0.002	0.2	<0.002	<0.0004	<0.04
Fe	1.5	0.25	2.62	1.75	10.5	0.344	0.229	1.38
Hg	0.01	0.25	0.0003	0.03	0.001	<0.0001	<0.01	<0.0004
K	30	23	2.9	0.097	0.126	8.8	0.293	0.383
La	1,700	†	<0.003	<0.000002	---	0.042	0.00002	---
Li	0.33	0.38	<0.1	<0.303	<0.263	0.2	0.606	0.526
Mg	90	87	11.1	0.123	0.128	11.6	0.129	0.133
Mn	0.25	0.10	0.221	0.884	2.2	0.024	0.096	0.24
Na	800	†	13.7	0.017	---	31.2	0.039	---
Ni	0.23	0.010	<0.04	<0.174	<4.0	<0.04	<0.174	<4.0
P	15	0.0005	<0.03	<0.002	<60.0	<0.03	<0.002	<60.0
Pb	0.25	0.05	<0.05	0.2	1	<0.05	<0.2	<1.0
Sb	7.5	0.2	<0.02	<0.003	<0.1	<0.02	<0.003	<0.1
Si	150	†	4.47	0.030	---	3.40	0.023	---
Sr	46	†	<0.350	0.008	---	0.342	0.007	---
V	2.5	0.15	0.003	0.001	0.02	<0.003	<0.001	<0.02
Zn	25	0.10	0.037	0.001	0.37	<0.007	<0.0003	<0.07

(Continued)

* Arsenic (As) and antimony (Sb) were determined by atomic absorption (Level 2), and mercury (Hg) by a cold vapor method (Level 1). All other elements were determined by ICP (Level 2).

† Ecology-based DMEG values have not been established.

TABLE 30 (Continued)

Element	Sump #6 Discharge			Carbide Lime Liquid			Bottom Ash Liquid		
	mg/l	Discharge Severity		mg/l	Discharge Severity		mg/l	Discharge Severity	
		Health	Ecology		Health	Ecology		Health	Ecology
Al	0.89	0.011	0.89	0.03	0.0004	0.03	0.05	0.0006	0.05
As	0.03	0.12	0.6	0.02	0.08	0.4	0.04	0.16	0.8
B	0.005	0.0001	0.0002	0.005	0.0001	0.0002	0.005	0.0001	0.0002
Ba	0.03	0.006	0.012	0.72	0.144	0.288	0.03	0.006	0.012
Ca	40.3	0.168	2.5	798	3.3	49.9	45.5	0.190	2.8
Cd	0.007	0.14	7.0	0.007	0.14	7.0	0.007	0.14	7.0
Co	0.016	0.021	0.064	0.009	0.012	0.036	0.011	0.015	0.044
Cr	0.01	0.04	0.04	0.01	0.040	0.040	0.01	0.040	0.040
Cu	0.012	0.002	0.24	0.005	0.001	0.1	0.005	0.001	0.1
Fe	2.28	0.52	9.12	0.028	0.019	0.112	0.206	0.137	0.824
Hg	0.0001	0.01	0.0004	0.0001	0.01	0.004	0.0001	0.01	0.0004
K	3.4	0.113	0.148	9.0	0.3	0.391	2.8	0.093	0.122
La	0.028	0.00002	---	0.195	0.0001	---	0.003	0.000002	---
Li	0.1	0.303	0.263	1.1	3.3	2.9	0.1	0.303	0.263
Mg	10.1	0.112	0.116	0.234	0.003	0.003	8.66	0.096	0.1
Mn	0.215	0.86	2.15	0.001	0.004	0.01	0.055	0.22	0.55
Na	31.3	0.039	---	49.0	0.061	---	12.1	0.015	---
Ni	0.04	0.174	4.0	0.04	0.174	4.0	0.04	0.174	4.0
P	0.03	0.002	60.0	0.03	0.002	60.0	0.03	0.002	60
Pb	0.05	0.2	1.0	0.05	0.2	1.0	0.05	0.2	1
Sb	0.02	0.003	0.1	0.02	0.003	0.1	0.02	0.003	0.1
Si	4.36	0.029	---	0.156	0.001	---	3.28	0.022	---
Sr	0.409	0.009	---	2.23	0.048	---	0.397	0.009	---
V	0.003	0.001	0.02	0.003	0.001	0.02	0.003	0.001	0.02
Zn	0.008	0.0003	0.08	0.007	0.0003	0.07	0.007	0.0003	0.07

Several ecological DMEG values are exceeded by large amounts in all five streams, including both streams discharging into the river. However, concentrations of almost all those elements in the sump #6 discharge exceeding DMEG ecology values are present at nearly the same concentrations as in the make-up water. These elements are Al, Ca, Cd, Fe, Mn, Ni, P, and Pb.

Those elements exceeding, or potentially exceeding, DMEG ecology values in the ash pond overflow are Ca, Cd, Fe, Ni, P, and Pb. The greatest potential ecological discharge problem appears to be phosphorus in both the ash pond overflow and the sump #6 discharge (discharge severity potentially as high as 60.0). Since P is typically the limiting nutrient in fresh waters, P discharges have the potential to greatly alter ecological characteristics of receiving waters. This is, however, only a potential problem, as the discharge severity is something less than 60.0, and may in fact be quite low.

Since bottom ash and fly ash are sluiced with river water, make-up water and bottom ash liquid show a similar elemental composition, and similar discharge severities. Ash pond overflow consists not only of these streams, but of ash and sludge from two other units at Cane Run. Assuming all units fire similar coal and that no chemical reactions occur to greatly increase or decrease elemental concentrations in the pond, the pattern of discharge severities in the make-up water, bottom ash liquid, and ash pond overflow should be similar. Calcium should be discharged at a higher concentration than in make-up water due to sludge from the other two units. This situation is born out by the data.

4.5.3 Organic Analyses

Concentrations of C_7-C_{16} organics and higher molecular weight ($>C_{16}$) organics measured in four of the liquid streams (make-up water, ash pond overflow, sump #6 discharge, bottom ash slurry) are summarized in Table 31. The high molecular weight fraction comprises most of the organic content. Concentrations of C_7 through C_{16} fractions exceed detection limits in only five instances, three of these in the sump #6 discharge. Total organic concentrations were greatest in the sump #6 discharge stream (0.283 to 0.290 mg/l), and least in the ash pond overflow (0.002 to 0.011 mg/l). The source

TABLE 31. ORGANIC ANALYSIS OF LIQUID STREAMS*

Carbon Number	Concentration, mg/l			
	Make-up Water	Ash Pond Overflow	Sump #6 Discharge	Bottom Ash Liquid
C_7	<0.001	<0.001	<0.001	<0.001
C_8	<0.001	<0.001	<0.001	<0.001
C_9	<0.001	<0.001	<0.001	<0.001
C_{10}	<0.001	<0.001	<0.001	0.001
C_{11}	<0.001	0.002	0.001	0.001
C_{12}	<0.001	<0.001	0.001	<0.001
C_{13}	<0.001	<0.001	0.001	<0.001
C_{14}	<0.001	<0.001	<0.001	<0.001
C_{15}	<0.001	<0.001	<0.001	<0.001
C_{16}	<0.001	<0.001	<0.001	<0.001
Total TCO	<0.010	0.002 to 0.011	0.003 to 0.010	0.001 to 0.010
Total GRAV	0.142	0.000	0.280	0.111
TCO + GRAV	0.142 to 0.152	0.002 to 0.011	0.283 to 0.290	0.112 to 0.121

*Level 1.

of organics in the sump #6 discharge may be oil from the pumps for the vacuum filters.

Analysis of make-up water, sump #6 discharge, and bottom ash liquid for POM showed traces of naphthalene at less than 6 µg/l in each stream. Naphthalene was present above the detection limit of about 1 µg/l, but below concentrations required for accurate quantitation. At 6 µg/l, the concentration of naphthalene is approximately five orders of magnitude less than the health-based DMEG of 750 mg/l, and more than one order of magnitude less than the ecology-based DMEG of 100 µg/l. No POM was detected in the ash pond overflow. The carbide lime liquid was not analyzed for POM.

4.6 SOLID WASTES AND PROCESS SOLIDS

Seven solid or slurry streams were sampled, including reheat oil, fly ash, soda ash, filter cake, economizer ash, carbide lime, and bottom ash. Of these, coal ash streams and filter cake are waste streams by design. Both inorganic and organic analyses performed on solid streams are presented in this section.

4.6.1 Inorganic Analyses

Concentrations of 25 elements are presented in Table 32, and sulfate analyses in Table 33. To assess the hazard potential of the waste streams, DMEG values for all elements are listed and discharge severities have been calculated for each discharge stream. Of the four streams discharged into the environment, the fly ash exceeds the most health DMEG values, four, including Al, As, Fe, and Mn. DMEG health values for iron are exceeded by all four streams and Al and Mn by three of the four. All four streams exceed DMEG ecology values for numerous elements.

It should be noted that due to the previously mentioned water balance problems, filter cake was not washed on the rotary drum filters. Therefore, the sodium (and probably sulfate) concentration in the filter cake is abnormally high.

4.6.2 Organic Analyses

Three of the solid streams, fly ash, filter cake, and economizer ash, were analyzed for organics. Concentrations of C_7-C_{16} organics and higher molecular weight organics (>C_{16}) measured in the solid wastes are presented

TABLE 32. MAJOR AND TRACE ELEMENT CONCENTRATIONS IN PROCESS AND WASTE SOLIDS

Element	DMEG Value, mg/kg		Fly Ash			Economizer Ash		
	Health	Ecology	mg/kg	Discharge Severity		mg/kg	Discharge Severity	
				Health	Ecology		Health	Ecology
Al	16,000	200	61,800	3.86	309	19,600	1.23	98
As	50	10	57	1.1	5.7	32.1	0.642	3.21
B	9,300	5,000	781	0.0840	0.156	290	0.0312	0.0580
Ba	1,000	500	170	0.170	0.340	359	0.359	0.718
Ca	48,000	3,200	2,480	0.0517	0.775	73,300	1.53	22.9
Cd	10	0.2	4.30	0.0430	21.5	<0.8	<0.08	<4
Co	150	50	25	0.17	0.50	25	0.17	0.50
Cr	50	50	43.8	0.876	0.876	9.6	0.19	5.0
Cu	1,000	10	42.6	0.0426	4.26	31.6	0.0316	3.16
Fe	300	50	140,000	467	2,800	209,000	697	4,180
Hg	2	50	0.047	0.024	0.00094	0.004	0.002	0.00008
K	No data	4,600	4,300	---	0.93	880	---	0.19
La	340,000	No data	<1	<0.001	---	<0.4	<0.001	---
Li	70	75	29	0.41	0.39	20	0.29	0.27
Mg	18,000	17,400	4,490	0.249	0.258	2,730	0.152	0.157
Mn	50	20	318	6.36	15.9	229	4.58	11.5
Na	160,000	No data	720	0.0045	---	170	0.0011	---
Ni	45	2	14	0.31	7.0	24	0.53	12
P	3,000	0.1	550	0.183	5,500	<3	<0.001	<30
Pb	50	10	<6	<0.1	<0.6	<6	<0.1	<0.6
Sb	1,500	40	<0.4	<0.0003	<0.01	<0.4	<0.0003	<0.01
Si	3,000	No data	<1	<0.0003	---	18	<0.0060	---
Sr	9,200	No data	<8	<0.0009	---	<8	<0.0009	---
V	500	30	172	8.34	5.73	48.8	0.0976	1.63
Zn	5,000	20	234	0.0468	11.7	153	0.0306	7.65

(Continued)

TABLE 32 (Continued)

Element	Bottom Ash			Filter Cake			Reheat Oil,	Soda Ash,	Lime,
	mg/kg	Discharge Severity		mg/kg	Discharge Severity		mg/kg	mg/kg	mg/kg
		Health	Ecology		Health	Ecology			
As	24,300	1.52	122	11,000	0.69	56	<3	34	8,590
As	13.1	0.262	1.31	6.2	0.12	0.62	<2	0.4	<Blank
B	54.7	0.00588	0.0109	346	0.0372	0.0692	<0.5	18	<0.6
Ba	48	0.048	0.096	<2	<0.002	<0.004	<3	<2	<2
Ca	25,200	0.525	7.88	198,000	4.13	61.9	3.69	<1	492,000
Cd	<0.8	<0.08	<4	<0.8	<0.08	<4	<0.7	<0.8	<0.8
Co	14	0.093	0.28	<1	<0.007	<0.02	<0.9	<1	<1
Cr	5.0	0.10	0.10	<1	<0.02	<0.02	<1	1.2	1.2
Cu	1.6	0.0016	0.16	<0.2	<0.0002	<0.02	<Blank	<0.2	6.1
Fe	39,400	131	788	9,870	32.9	197	<Blank	14	2,820
Hg	<0.02	<0.01	<0.0004	0.198	0.0990	0.00396	0.09	0.016	0.059
K	910	---	0.20	620	---	0.13	10	428	65
La	<0.4	<0.001	---	<1	<0.001	---	<0.3	0.4	17
Li	9.3	0.14	0.013	12	0.17	0.16	<10	<2	26
Mg	3,200	0.0178	0.141	8,000	0.444	0.460	<Blank	4	11,800
Mn	358	7.16	17.9	47	0.94	2.4	<0.1	<0.1	178
Na	280	0.0018	---	8,230	0.0514	---	<10	473,000	22
Ni	<4	<0.09	<2	<4	<0.09	<2	<Blank	<4	<4
P	241	0.0803	2.41	<3	<0.001	<30	<3	<3	<3
Pb	<6	<0.1	<0.6	<6	<0.01	<0.6	<5	14	<6
Sb	<0.4	<0.0003	<0.01	<0.4	<0.0003	<0.01	<2	<0.4	<0.4
Si	<1	<0.0003	---	<1	<0.0003	---	<1	48	<1
Sr	<8	<0.0009	---	<8	<0.0009	---	<7	<8	<8
V	48.3	0.0966	1.61	19	0.038	0.63	<0.3	<0.4	<4
Zn	76.5	0.0153	3.83	48.7	0.00974	2.44	<Blank	<0.8	42.5

TABLE 33. SULFATE ANALYSIS OF PROCESS AND WASTE SOLIDS

Stream Name	Sulfate Concentration, mg/kg	Discharge Severity Health
Fly Ash	9,590	0.0384
Filter Cake	28,600	0.114
Economizer Ash	6,570	0.0263
Lime	4,820	0.0193
Bottom Ash	1,190	0.0048

in Table 34. Total organics in the filter cake consisted primarily of higher molecular weight organics while the fly ash and economizer ash contained more organics in the C_7-C_{16} range.

Traces of naphthalene (<50 µg/kg) were detected in the fly ash by GC/MS. The filter cake contained 910 µg/kg of naphthalene, and 190 µg/kg of phenanthrene, as well as traces (<100 µg/kg) of the following compounds: biphenyl, acenaphthalene, dimethylnaphthalenes, fluorene, benzo(c)cinnolene, phenanthrenedione, dibenzothiophene, methylphenanthrene, fluoranthene, pyrene, and crysene. The detection limit for individual compounds was approximately 20 µg/kg.

TABLE 34. ORGANIC ANALYSES OF SOLID WASTES

Carbon Number	Concentration, mg/kg		
	Fly Ash (ESP)	Filter Cake	Economizer Ash
C_7	<0.001	<0.001	<0.001
C_8	0.010	0.026	0.009
C_9	0.148	0.380	<0.001
C_{10}	0.011	0.036	0.005
C_{11}	0.039	0.036	<0.001
C_{12}	0.015	1.207	0.005
C_{13}	0.014	0.160	0.004
C_{14}	0.018	0.226	0.008
C_{15}	0.015	0.180	0.006
C_{16}	0.013	0.052	0.003
Total TCO	0.283	2.303	0.040
Total GRAV	0.197	16.92	0.000
TCO + GRAV	0.480	19.22*	0.040

*This sample exceeds the 1.0 mg/kg criterion for LC; however, the TCO + GRAV total for the 0.464 kg sample extracted was 8.92 mg, less than the 15 mg minimum sample size recommended for LC by the Level 1 Procedures Manual.

REFERENCES

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APPENDIX A

ANALYTICAL PROCEDURES APPLIED TO CANE RUN SAMPLES

With a few exceptions discussed below, the samples were prepared and extracted according to the procedures in Emissions Assessment of Conventional Stationary Combustion Systems: Methods and Procedures Manual for Sampling and Analysis (EACCS), EPA-600/7-79-029a. The overall inorganic analysis scheme is presented in Figure A-1 and the organic analysis scheme in Figures A-2 and A-3. The numerical references in Figures A-2 and A-3 are references to the EACCS manual.

Inorganic Analyses

Most trace elements were analyzed by Inductively Coupled Optical Emission Spectroscopy (ICP). ICP is a flame emission technique in which atoms are thermally excited to emit light at their characteristic wavelengths. In practice, samples in the form of a liquid are aspirated into the atomizer. The atomization and excitation source is a plasma torch whose temperature is on the order of 7000°K. The entire instrument is controlled by a mini-computer, which can store calibration curves and calculate solution concentrations directly. Sensitivities are on the order of 0.1 µg/ml to 1.0 µg/ml. These analyses are vended and analytical procedures are not detailed here.

ICP was supplemented with cold vapor UV analysis for mercury (EACCS 8.4) and graphite furnace atomic absorption analyses using standard addition for arsenic and antimony (Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants, April 1977, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268). The graphite furnace method was selected for these samples because of its better sensitivity than the hydride generation method.

Aqua regia digestion (EACCS 8.2.2) was used to prepare most solids for trace element analysis. The XAD-2 resin and product sulfur were prepared by Paar bomb combustion (EACCS 8.2.1), and the coal by low temperature plasma ashing followed by HF-HNO_3 Paar bomb combustion.

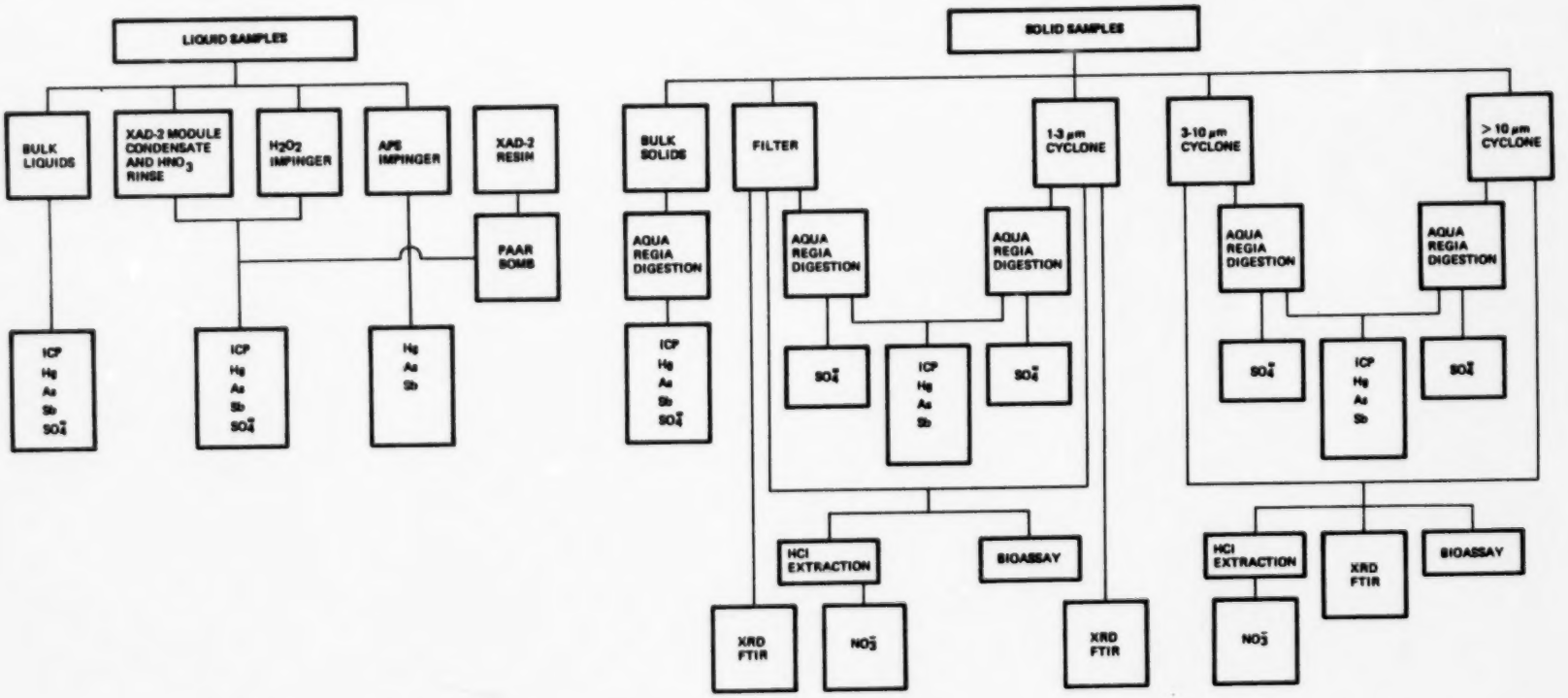

Figure A-1. Inorganic Analyses Flow Chart

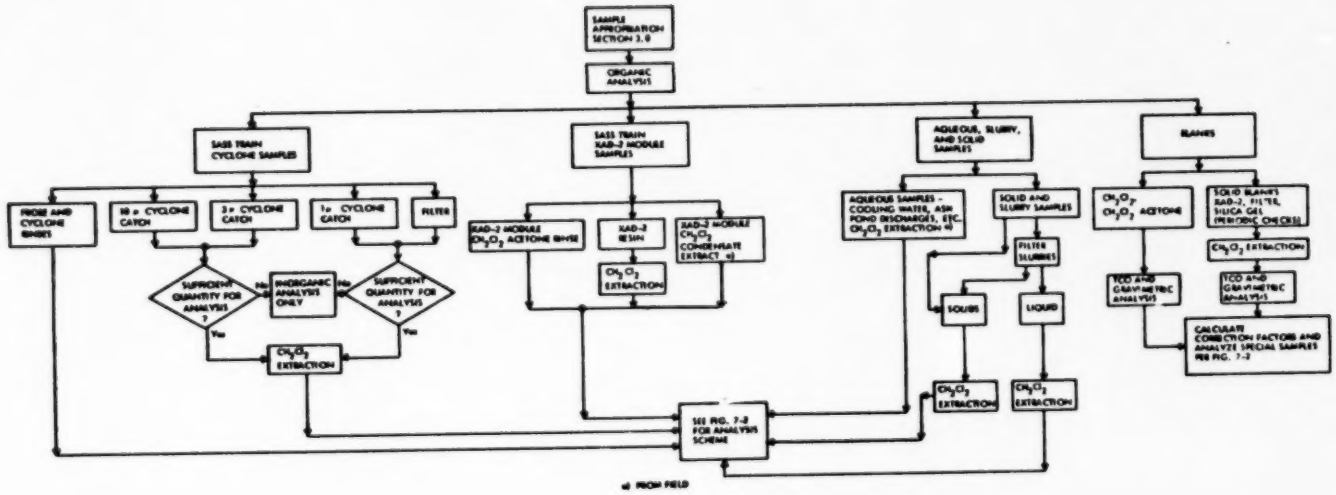

Figure A-2. Level 1 Organic Analysis Flow Chart

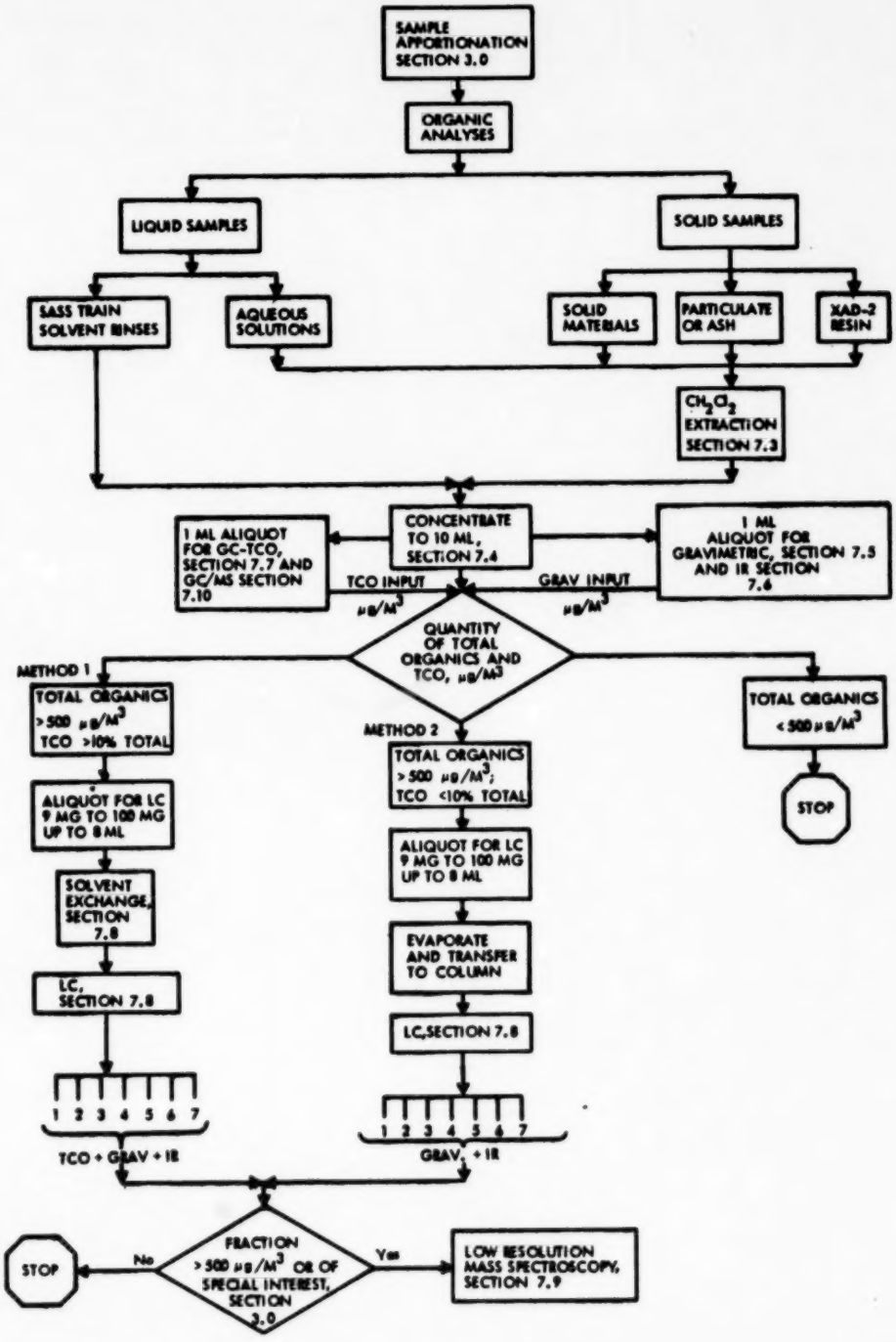

Figure A-3. Level 1 Organic Analysis Methodology

An aliquot of each SASS particulate aqua regia digestate was used for sulfate analysis by ion chromatograph (IERL-RTP Procedures Manual: Level 1 Environmental Assessment, EPA-600/7-78-201). Sulfate analyses on bulk solids and liquids were also performed by ion chromatography.

The hydrochloric acid extraction procedure used for preparation of SASS particulate samples for nitrate analysis was the same as EACCS 8.8.2, with the exception that 0.01M HCl was used. Nitrate was analyzed by ultraviolet spectrophotometry (Method 419 A, Standard Methods for the Examination of Water and Wastewater, 14th ed.).

Controlled Condensation Sampling Train (CCS) samples were analyzed by ion selective electrode for fluoride (EACCS 8.9) and chloride (EACCS 8.10) and by the turbidimetric sulfate procedure (EACCS 8.7).

All MRI impactor sulfate analyses were by ion chromatography. The procedure for removal of the sulfate from the Apiezon-coated impactor plates was developed recently at TRW, and details are given in Appendix B.

The powder X-ray diffraction (XRD) analysis is described in the EPA/IERL-RTP Procedures Manual: Level 2 Sampling and Analysis of Oxidized Inorganic Compounds, EPA-600/2-79-200, Section 3.2. A description of Fourier Transform Infrared (FTIR) methodology is given in the same manual, Section 3.1.

Organic Analyses

Samples acquired at Cane Run No. 6 were analyzed in accordance with the EACCS Methods and Procedures Manual (EPA-600/7-79-029a).

Bioassay

All SASS bioassay samples were returned to TRW for preparation prior to testing by the bioassay contractor. Samples were collected over six days at three locations: the ESP outlet and the outlet to both scrubber modules. Flue gas volumes samples were approximately 40 dscm for each test at each location. Three types of sample components were obtained from each location:

- XAD-2 resin extracts
- Filter catches
- Cyclone catches

The entire 150 g of XAD-2 resin from each test was extracted and concentrated using the normal procedure (EACCS 7.4). Extracts from both scrubber outlet samples were composited into a single outlet sample for each day. Filter and cyclone catches were weighed to constant weight.

Filter catches at the ESP outlet were composited as follows: 12-10 with 12-11, 12-13 with 12-14, and 12-15 with 12-16. Scrubber outlet filter catches were not composited.

At the ESP outlet, all three cyclones (10 μm, 3 μm, and 1 μm) were used. Catches for each cyclone were composited into two samples: one for tests on 12-10 through 12-14 and another for tests on 12-15 and 12-16 (total of six composites). At the FGD outlet, only the 3 μm cyclone was used. Catches from both modules were composited for the same test days as ESP outlet cyclone samples (total of four composites).

Two grab samples each of three liquid streams - ash pond overflow, sump #6 discharge, and bottom ash slurry - were collected for bioassay. Each sample was 13 gallons.

Solid samples of fly ash and filter cake were also collected for bioassay.

APPENDIX B

PROCEDURES FOR ANALYSIS OF SULFATE ON MRI IMPACTOR PLATES

EQUIPMENT

(1) Petri Dishes; obtain 7 small (50 mm diameter) petri dish covers or bottoms and mark them sequentially, using a diamond stylus or vibrating etcher. Do not use pencil or grease pen as they will be removed during plasma ashing.

(2) Low Temperature Plasma Asher (LTA); International Plasma Corporation Model PM104B unit or equivalent.

(3) Drying Oven; capable of 100°C ± 5°C.

(4) Steam Bath.

REAGENTS

(1) Toluene; ACS reagent grade minimum.

(2) Sodium Carbonate Solution; dissolve 40 gms of Na_2CO_3 in 1 liter of deionized water. 1.0 ml = 40 mg Na_2CO_3.

(3) Hydrochloric acid; 0.01 M HCl; 0.83 ml conc. HCl diluted to 1 liter.

CLEANING

It is very important that all glassware used in this procedure be precleaned with 1+1 HCl acid. Special emphasis should be given to the cleaning of the petri dishes, since both internal and external surfaces may be contacted by the extracting solvent.

PROCEDURE

(1) Perform all extractions and evaporations of toluene in fume hood and do not allow open flames in the work area.

(2) Turn on steam bath (low or med. heat) inside fume hood, allowing it to heat while carrying out the following steps. Adjust drying oven to 80°C ± 5°C.

(3) Obtain a group of impactor discs; for optimum organization it is suggested that the discs are handled in groups of seven, as they are arranged in the impactor assembly.

(4) Carefully pipet 1.0 ml of toluene, using a disposable Pastuer pipet, into each of the impactor discs to dissolve the Apiezon L grease. Allow the toluene to contact the discs, inside the designated petri dish, for about a minute.

(5) Carefully transfer the toluene - Apiezon L solution from the impactor disc into the appropriate petri dish, rinsing the disc with two 1.0 ml volumes of toluene.

(6) Add another portion of toluene, as in Step 4, to impactor disc.

(7) Transfer, as in Step 5.

(8) Repeat the dissolution and transfer steps until the Apiezon L grease and any particulate material is completely transferred from the impactor disc into the petri dish. If any remaining Apiezon L grease adheres to the disc, scrape with a stainless steel or teflon spatula (<u>not</u> a rubber policeman) and rinse again with toluene.

(9) Gently warm the petri dish containing the toluene - Apiezon L solution over a steam bath until the solvent has completely evaporated. Rotate the petri dish while evaporating the toluene to create an even layer of Apiezon L and particulate. (Caution: do not overheat, as this will cause Apiezon L to darken).

(10) Add 1.0 ml of 40 mg/ml Na_2CO_3 solution to each petri dish and distribute the solution evenly over the Apiezon covered portion of the internal surface. Dry in an 80°C oven until the water has evaporated.

(11) Following the instructions supplied in the instrument operating manual, tune the low temperature plasma asher to optimize operation.

(12) Remove the prepared petri dishes from the drying oven and allow to cool.

(13) Place the cooled petri dishes in the low temperature plasma asher and subject them to low temperature ashing for 24 hours or until the Apiezon L is completely oxidized.

(14) When ashing step has been completed, carefully remove the petri dishes from LTA and allow to cool. The ash produced in this step is very light and is easily lost if exposed to air currents.

(15) Carefully rinse the ash from the petri dish into a 150 ml beaker, using 50 ml of 0.01 M HCl.

(16) If the ash adheres to the internal surface of petri dish, the entire dish may be submerged in 0.01 M HCl, in a 250 ml beaker, to accomplish dissolution.

(17) After bringing the 0.01 M HCl solution to a gentle boil, cover beaker with a watch glass, and allow to boil for 2 hours. It will be necessary to add deionized water to maintain the proper volume.

(18) Make note of any suspended or insoluble material observed during and after digestion.

(19) When digestion is completed, remove beaker from hot plate and cool. Filter sample with a #41 Whatman filter pad and dilute to a volume of 50.0 ml.

(20) Determine sulfate on the sample extract using ion chromatography.

(21) Blanks and standards (produced by pipetting a standard Na_2SO_4 solution onto unused impactor plates) should be run with the first group of samples and every fifth group thereafter.

(22) Calculations:

$$\text{mg sulfate} = A \times B$$

where A = ppm sulfate in solution

B = final solution volume from Step 19, Liters).

APPENDIX C

RESULTS OF INFRARED ANALYSES

TABLE C-1. SUMMARY OF INFRARED ANALYSES ON FLUE GAS SAMPLES

	Sample		
	ESP Inlet	ESP Outlet	Scrubber Outlet
Original Sample	aliphatic hydrocarbons, substituted aromatics, fused ring aromatics, esters	aliphatic hydrocarbons, substituted aromatics, fused ring aromatics, esters	aliphatic hydrocarbons, substituted aromatics, fused ring aromatics, esters, possible heterocyctic aromatics
LCI	aliphatic hydrocarbons, aromatics, traces of silicones	aliphatic hydrocarbons	aliphatic hydrocarbons
LC2	*	*	subtituted benzene hydrocarbons
LC3	*	aliphatic esters	heterocyclic nitrogen compounds
LC4	*	esters, ethers, fused ring aromatics	heterocyclic nitrogen compounds, esters, ethers, ketones
LC5	*	fused ring aromatics, esters, phthalate esters	heterocyclic oxygen compounds, esters, ketones
LC6	phenols, esters, alcohols	alcohols, phenols, carboxylic acids	heterocyclic oxygen compounds, ketones, ethers
LC7	phenols, esters, alcohols	phenols, carboxylic acids	esters, ketones, carboxylic acids and derivatives

*Did not meet weight criterion for IR analysis (Grav. >0.5 mg).

TABLE C-2 INTERPRETATION OF INFRARED SPECTRA OF SAMPLE CONCENTRATES

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
167-XMCD-SE-KD-GI ESP Inlet	3210	W	OH	
	3060	W	Unsaturated CH	
	2958	M	Saturated CH	
	2920	M	Saturated CH	
	2852	M	Saturated CH	
	1720	M	Esters, broad C=O region	
	1602	W	Aromatic, C=C	
	1552	W	Fused Ring Breathing	
	1455	W	Saturated CH	
	1378	W	Saturated CH	
	1280	W	Ester, phenol, C-O	
	1260	W	Ester, phenol, C-O	
	1100	W	Ether, C-O	
	800	W	CH deformation in Aromatic Rings	
	750	W	CH deformation in Aromatic Rings	
	700	W	CH deformation in Aromatic Rings	
168-XMCD-SE-KD-GI ESP Outlet	3220	W	OH	
	3030	W	Unsaturated CH	
	2962	M	Saturated CH	
	2925	M	Saturated CH	
	2862	M	Saturated CH	
	1720	M	Esters, Broad C=O region	
	1605	W	Aromatic, C=C	
	1550	W	Fused Ring Breathing	
	1450	W	Saturated CH	
	1372	W	Saturated CH	
	1270	W	C-O, ester, phenol	
	1100	W	Ether, C-O	
	940	W	CH deformation in Aromatic Rings	
	800	W	CH deformation in Aromatic Rings	
	760	W	CH deformation in Aromatic Rings	
	705	W	CH deformation in Aromatic Rings	

(Continued)

TABLE C-2 (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
169-XMCD-SE-KD-GI	3400	W	Water, OH	Broad
Scrubber Outlet	3050	W	Unsaturated CH	
	2958	S	Saturated CH	
	2922	S	Saturated CH	
	2852	S	Saturated CH	
	1720	M	C=O, Esters	Broad
	1630	W	Aromatic	
	1602	W	Aromatic	
	1552	W	Ring breathing, fused rings, shape and intensity indicate heterocyclic	
	1460	W	Saturated CH	
	1378	W	Saturated CH	
	1278	W	C-O, ester, phenol	
	1100	W	Ether, C-O	
	860	W	CH deformation in Aromatic Rings	
	750	W	CH deformation in Aromatic Rings	
167/9-XRB-SE-KD-GI	2960	W	Saturated CH	
XAD-2 Resin Blank	2922	W	Saturated CH	
	2860	W	Saturated CH	
	1720	W	Esters, C=O	
	1455	W	Saturated CH	
	1372	W	Saturated CH	
	1349	W	Saturated CH	
	1265	W	C-O	
	1105	M	Ether, C-O	
167/9-14-OR-SE-KD-GI	3340	W	Water	Weak
Filter Cake	2952	W	Saturated CH	
	2920	M	Saturated CH	
	2850	M	Saturated CH	
	1675	W	Water	Broad
	1460	W	Saturated CH	
	1378	W	Saturated CH	

TABLE C-3 INTERPRETATION OF INFRARED SPECTRA OF LIQUID CHROMATOGRAPHY FRACTIONS

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
167-XMCD LC #1	2958	M	Saturated CH	
	2922	S	Saturated CH	
	2852	M	Saturated CH	
	1460	M	Saturated CH	
	1378	M	Saturated CH	
	1260	W	$Si(-CH_3)_n$ Silicones	
	1100	W	Si-O Silicones	
	1030	W	Si-O Silicones	
	800	W	$Si(-CH_3)_n$	
	718	W	Aromatic Hydrocarbons	
	695	W	Aromatic Hydrocarbons	
167-XMCD LD #6	3400	W	Water, OH	Broad
	3030	W	Aromatic CH	
	2960	M	Saturated CH	
	2922	M	Saturated CH	
	2860	M	Saturated CH	
	1720	W	C-O, Esters	
	1602	W	Aromatic, C=C	
	1550	W	Fused Ring Breathing	
	1450	W	Saturated CH	
	1375	W	Saturated CH	
	1270	W	Esters and phenols, doublet	
	1250	W	Esters and phenols, doublet	
	1100	M	Ether, C-O	
	950	W	Hydrogens on C=C	
	800	W	Hydrogens on C=C	
	752	W	Aromatic Ring	
	702	W	Aromatic Ring	
167-XMCD LC #7	3400	W	Water, OH	
	2960	M	Saturated CH	
	2922	M	Saturated CH	
	2860	M	Saturated CH	
	1725	W	Esters, C=O	
	1608	W	Aromatic	
	1450	W	Saturated CH	
	1410	W	Saturated CH	
	1370	W	Saturated CH	
	1250	W	C-O, ester, phenol	
	1100	S	C-O, ether	
	940	W	Aromatic	

(Continued)

TABLE C-3 (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
168-XMCD LC #1	2958	M	Saturated CH	Weak Scan
	2920	M	Saturated CH	
	2850	M	Saturated CH	
	1460	W	Saturated CH	
	1375	W	Saturated CH	
168-XMCD LC #3	2960	W	Saturated CH	Weak Scan
	2920	M	Saturated CH	
	2850	W	Saturated CH	
	1722	W	C=O, esters	
	1450	W	Saturated CH	
	1270	W	C-O, ester	
	1105	W	C-O, ether	
168-XMCD LC #4	2960	W	Saturated CH	Weak Scan
	2922	W	Saturated CH	
	2858	W	Saturated CH	
	1722	M	C=O, esters	
	1600	W	Aromatic	
	1550	W	Aromatic	
	1450	W	Saturated CH	
	1375	W	Saturated CH	
	1272	W	C-O, $Si(CH_3)_n$ (Silicones)	
	1120	W	C-O, Si-O	
	1070	W	C-O, Si-O	
	800	W	$Si(-CH_3)_n$	
	760	W	Aromatic Rings	
	710	W	Aromatic Rings	
168-XMCD LC #5	3440	W	Water, OH	Broad
	3060	W	Unsaturated CH	
	3020	W	Unsaturated CH	
	2960	M	Saturated CH	
	2922	M	Saturated CH	
	2860	M	Saturated CH	
	1720	M	Esters, C=O	
	1600	W	Aromatic, C=C	
	1550	W	Aromatic, Fused ring breathing	
	1480	W	Saturated CH	
	1450	W	Saturated CH	
	1368	W	Saturated CH	

(Continued)

TABLE C-3 (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
168-XMCD LC #5 (Continued)	1270	W	C-O, esters, phthalate esters	
	1175	W	C-O, esters, phthalate esters	
	1118	W	C-O, esters, phthalate esters	
	1070	W	C-O, esters, phthalate esters	
	1025	W	C-O, esters, phthalate esters	
	798	W	Aromatic Rings	
	750	W	Aromatic Rings	
	705	W	Aromatic Rings	
168-XMCD LC #6	3300	W	Water, OH, acid	Broad
	3030	W	Aromatic CH	
	2960	M	Saturated CH	
	2922	M	Saturated CH	
	2862	M	Saturated CH	
	1720	M	Esters, broad C=O	
	1700	M	C=O, acid	Shoulder on 1720
	1602	W	Aromatic, C=C	
	1550	W	Fused ring breathing	
	1450	W	Saturated CH	
	1412	W	Saturated CH; or coupling of acid C-O stretched and O-H bend	
	1368	W	Saturated CH	
	1270	W	C-O, ester, phenol	
	1180	W	C-O, ester, phenol	
	1100	W	Ether, C-O	
	940	W	Aromatic hydrocarbons; or O-H out-of-plane bending of acid	
	860	W	Aromatic hydrocarbons	
	800	W	Aromatic hydrocarbons	
	760	W	Aromatic hydrocarbons	
	710	W	Aromatic hydrocarbons	

(Continued)

TABLE C-3 (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
168-XMCD LC #7	3340	W	Water, OH	Broad
	2960	M	Saturated CH	
	2922	M	Saturated CH	
	2862	M	Saturated CH	
	1720	M	C=O, esters, acids	
	1602	W	Aromatic	
	1550	W	Aromatic, COO^-, acids, coupling of acid C-O stretch and O-H bend	
	1450	W	Saturated CH	
	1410	W	Saturated CH; COO^-, acids, coupling of acid C-O stretch and O-H bend	
	1370	W	Saturated CH	
	1270	W	Phenol doublet	
	1255	W	Phenol doublet	
	1105	M	Ether, C-O	
	940	W	Aromatic hydrocarbon	
	860	W	Aromatic hydrocarbon; or O-H out-of-plane bending of acid	
	800	W	Aromatic hydrocarbon	
	760	W	Aromatic hydrocarbon	
	712	W	Aromatic hydrocarbon	
169-XMCD LC #1	3040	W	Unsaturated CH	
	2960	S	Saturated CH	
	2922	S	Saturated CH	
	2858	S	Saturated CH	
	1705	W	Ester	Very weak
	1630	W	Aromatic C=C Skeletal ring	
	1600	W	Aromatic C=C	
	1460	M	Saturated CH	
	1378	M	Saturated CH	
	1300	W	$(CH_3)_2$-C, CH deformation	
	1275	W	$(CH_3)_2$-C, CH deformation	
	962	W	Aromatic hydrocarbons	
	870	W	Aromatic hydrocarbons	
	810	W	Aromatic hydrocarbons	
	740	W	Aromatic hydrocarbons	
	720	W	Aromatic hydrocarbons	

(Continued)

TABLE C-3 (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
169-XMCD LC #2	3020	W	Unsaturated CH	
	2958	M	Saturated CH	
	2922	M	Saturated CH	
	2852	M	Saturated CH	
	1712	W	C=O, ester	
	1700	W	C=O, ketone	
	1630	W	Aromatic	
	1600	W	Aromatic	
	1550	W	Ring breathing on Fused Rings, shape and intensity indicate heterocyclic ring	
	1455	W	Saturated CH	
	1375	W	Saturated CH C-$(CH_3)_n$ - CH deformation	
	1275	W	C-O	
	1198	W		
	852	W	Aromatic hydrocarbons	
	810	W	Aromatic hydrocarbons	
	745	W	Aromatic hydrocarbons	
	698	W	Aromatic hydrocarbons	
169-XMCD LC #3	3450	W	Water, trace	
	2958	M	Saturated CH	
	2922	S	Saturated CH	
	2852	M	Saturated CH	
	1738	W	Esters, C=O	
	1710	W	Ketones, C=O	
	1630	W	Phenols	
	1600	W	Aromatic	
	1550	W	Aromatic, Ring Breathing in heterocyclics, quinoline	
	1460	W	Saturated CH	
	1374	W	Saturated CH	
	1272	W	Esters, C-O	
	1198	W	Esters, C-O	
	860	W	Aromatic hydrocarbons	
	752	W	Aromatic hydrocarbons	
	700	W	Aromatic hydrocarbons	

(Continued)

TABLE C-3 (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
169-XMCD LC #4	3400	W	Water, OH	
	2958	M	Saturated CH	
	2922	M	Saturated CH	
	2852	M	Saturated CH	
	1740		C=O, aldehyde	
	1710	M	C=O, esters	
	1700	M	C=O, ketone	
	1630	W	Aromatic	
	1602	W	Aromatic	
	1550	W	Aromatic, heterocyclic O-quinolines	
	1455	W	Saturated CH	
	1375	W	Saturated CH	
	1275	W	Ester, C-O	
	1120	W	Ester, C-O	
	1070	W	Ether, C-O	
	755	W	Aromatic rings	
	700	W	Aromatic rings	
169-XMCD LC #5	3400	W	Water, OH	Broad
	2960	S	Saturated CH	
	2922	S	Saturated CH	
	2860	M	Saturated CH	
	1710	M	C=O Esters, ketones, aldehydes	Broad peak
	1630	W	C=O Esters, ketones, aldehydes	Broad peak
	1602	W	Aromatic	
	1550	M	Aromatic heterocyclic -O, CH	
	1460	W	Saturated CH	
	1450	W	Saturated CH	
	1378	W	Saturated CH	
	1280	W	Ester, C-O	
	755	W	Aromatic rings	
	700	W	Aromatic rings	

(Continued)

TABLE C-3 (Continued)

Sample	Band Location cm^{-1}	Band Intensity	Assignment	Comments
169-XMCD LC #6	3400	W	Water, OH	Broad
	2960	M	Saturated CH	
	2922	M	Saturated CH	
	2862	M	Saturated CH	
	1710	M	Esters, ketones	Broad
	1630	W		
	1602	W	Aromatic	
	1550	W	Aromatic, shape and intensity indicate heterocyclic O	
	1450	W	Saturated CH	
	1378	W	Saturated CH	
	1270	W	C-O, ester	
	1100	W	Ether, C-O	
	760	W	Aromatic rings	
	710	W	Aromatic rings	
169-XMCD LC #7	3400	W	Water, OH	Broad
	2960	M	Saturated CH	
	2922	M	Saturated CH	
	2870	M	Saturated CH	
	1720	W	Esters	
	1710	W	Ketones, acids	
	1600	W	Aromatic	
	1552	W	Fused ring breathing, COO^- acids	
	1462	W	Saturated CH	
	1450	W	Saturated CH	
	1372	W	Saturated CH	
	1252	W	C-O	
	1100	S	Ether	
	945	W	Aromatic hydrocarbons	
	850	W	Aromatic hydrocarbons	
	755	W	Aromatic hydrocarbons	

APPENDIX D

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) ANALYSIS OF FLUE GAS PARTICULATE SAMPLES FROM CANE RUN

Particulate samples collected with the SASS train at the Louisville Gas & Electric Company's Cane Run No. 6 boiler/FGD system were analyzed by a Nicolete 7000 FTIR for specific compound identification. FTIR was used over conventional IR techniques because it has improved sensitivity and data manipulation capabilities. Because FTIR uses an interferometer rather than a monochrometer to separate wavelengths, an interferogram is produced and then reduced to a wavelength vs. energy plot using a Fourier Transform. The spectra produced in this fashion are digitalized and can be stored in a computer for later manipulation. During this program, spectra of $NaHCO_3$, $NaHSO_4$, Na_2CO_3, $NaHSO_3$, Na_2SO_3, and $CaSO_4$ were stored in the computer and were available for electronic addition to the sample spectra. This "spiking" procedure facilitates the identification of IR bands associated with any of those compounds.

One milligram aliquots of loose particulate samples were mixed with 2.5 g of KBr in an agate mortar and pestle. Using a vacuum press, these samples were pressed into 10 mm diameter pellets of approximately 1 mm thickness. It was originally planned to obtain spectra of the particulate matter impacted on the glass fiber filter using a KRS-5 ATR cell. The filter background would then be subtracted from the sample spectra using the FTIR computer. Although this procedure worked well in the past, poor quality spectra were obtained. Most of the filter samples had a layer of impacted particulate matter which could be removed using a scalpel. If not, a small amount of the glass fiber filter was removed with the particulate matter and placed in a KBr pellet. The sample was then run on the FTIR and the glass fiber filter spectrum was subtracted from the sample spectrum to leave only the bands associated with the particulate matter. All samples were run from 400 to 4000 cm^{-1}. Table D-1 lists the samples analyzed.

TABLE D-1. PARTICULATE SAMPLES ANALYZED BY FTIR

Location	Sample Number	Description*
ESP Inlet	167-CC	3 μm and 10 μm cyclone catches
	167-1C	1 μm cyclone catch
	167-PF	Particulate filter catches
ESP Outlet	168-CC	3 μm and 10 μm cyclone catches
	168-FC	1 μm cyclone and filter catches
Scrubber Outlet	169-CC	3 μm and 10 μm cyclone catches
	169-FC	1 μm cyclone and filter catches

*CC catches were ratioed by the weights of each catch and composited.

The standard approach was to look at the FTIR spectra in the region of 400-1400 cm^{-1}, primarily focusing on the 400 to 900 cm^{-1} region. This is where most of the inorganic bands lie. Typically anion types (sulfate, oxide) were recognized first. Comparison of the unknown spectra to spectra of standards prepared by TRW (Figures D-1 through D-6) or to reference spectra (Nyquist and Kagel "Infrared Spectra of Inorganic Compounds") aided in the exact compound identification. Additional guidance was provided by the elemental data for the SASS Level 1 particulate catches. The spectra were generally very weak. Without the stability of FTIR and its computer-assisted spectra magnification, little or no information would have been obtained.

One problem in identifying fly ash components is that mineral matter present in the coal often has an amorphous structure after firing; this tends to hamper clear identification of the original mineral. In cases where bands appear in regions known for silicate minerals, a general term "silicate matrix" will be applied. A discussion of each sample follows and their IR spectra from 400 to 900 cm^{-1} are presented.

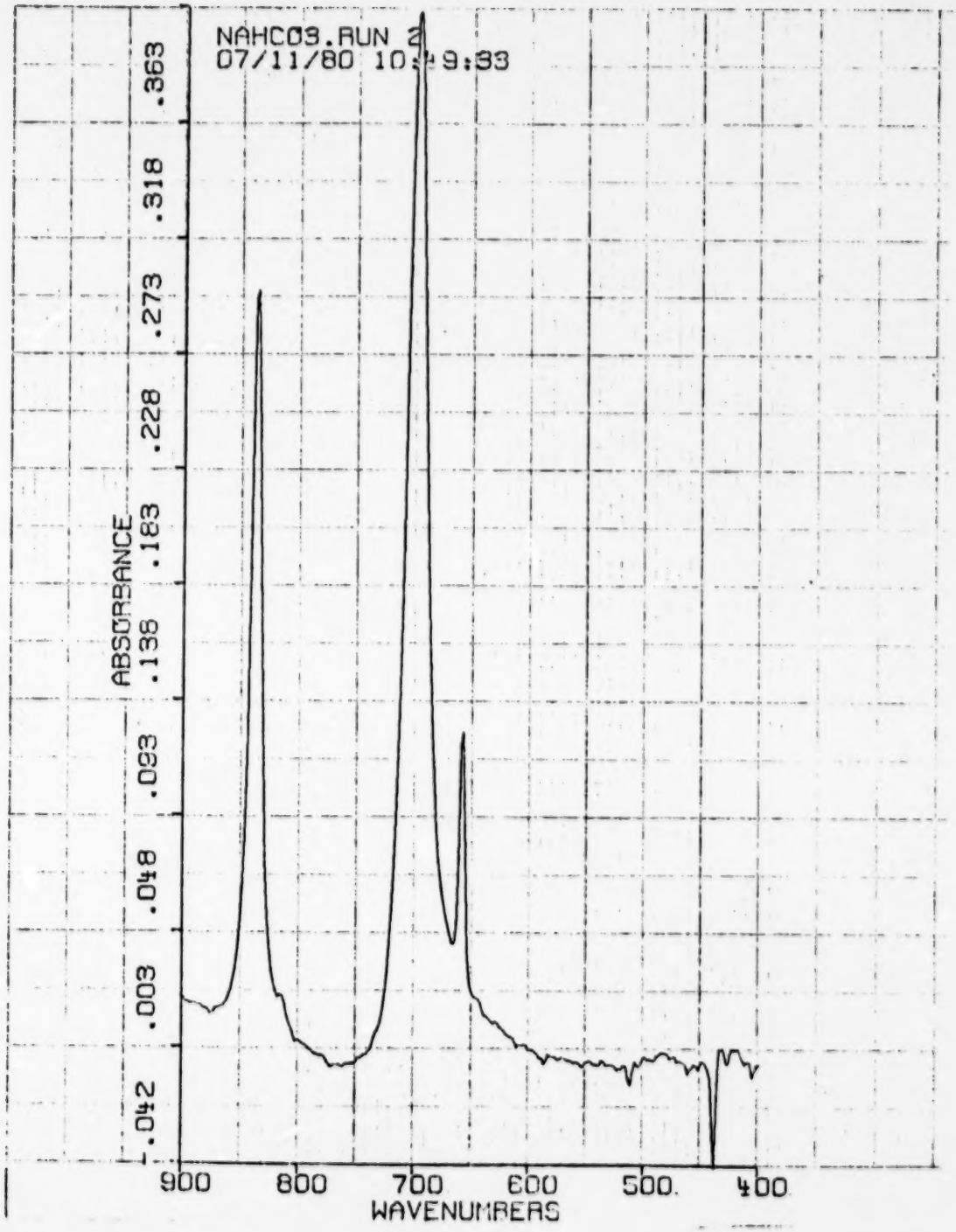

Figure D-1. Sodium Bicarbonate Standard

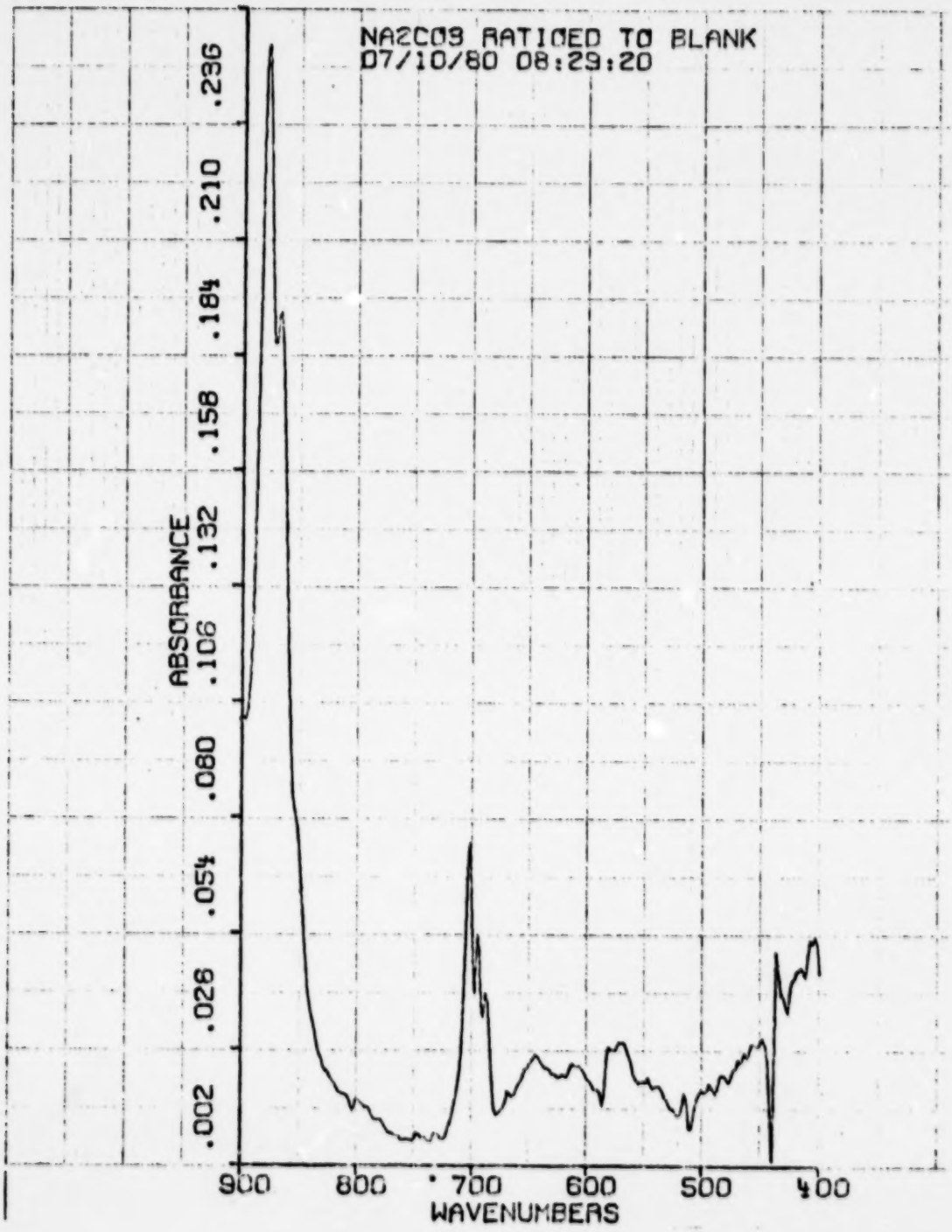

Figure D-2. Sodium Carbonate Standard

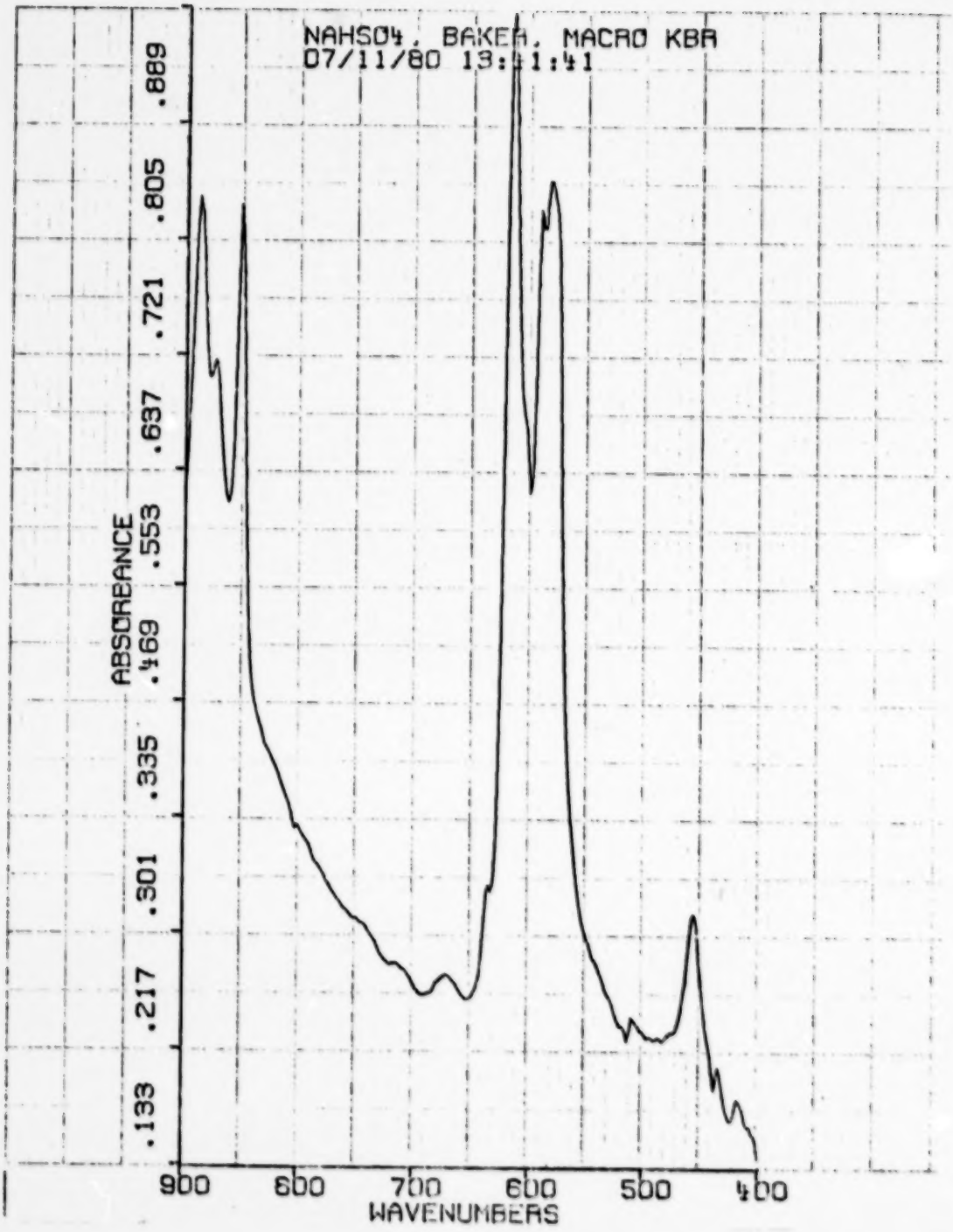

Figure D-3. Sodium Bisulfate Standard

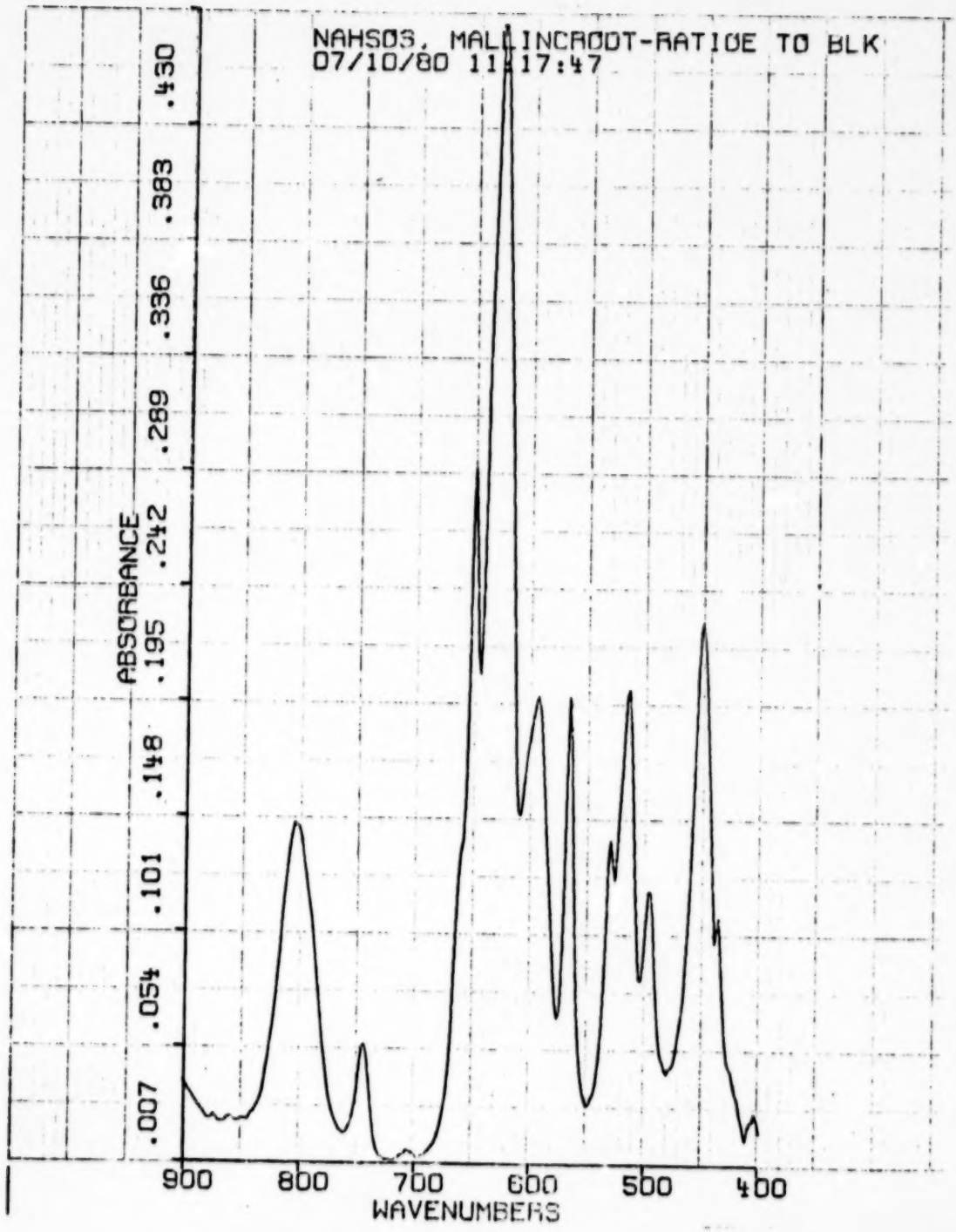

Figure D-4. Sodium Bisulfite Standard

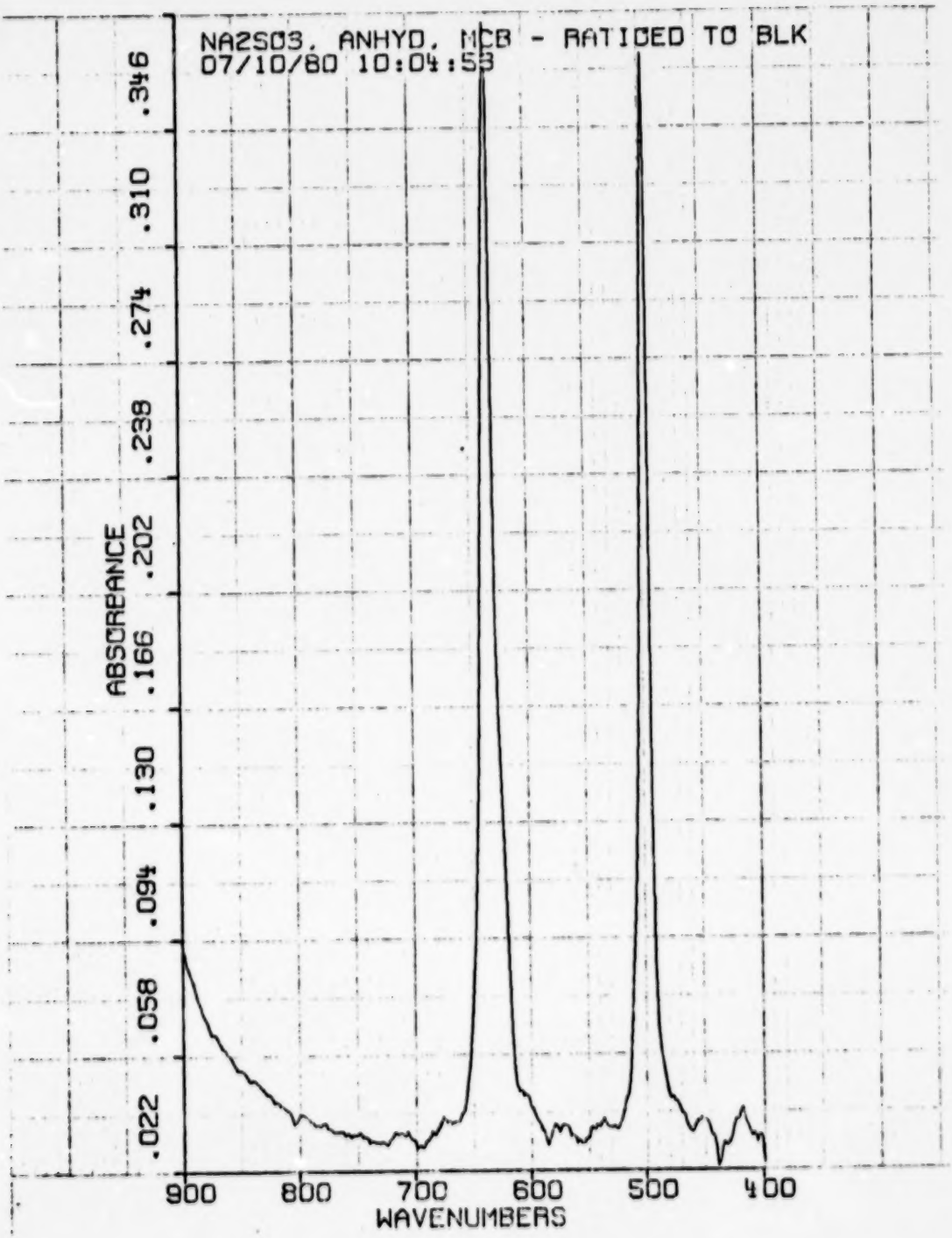

Figure D-5. Sodium Sulfite Standard

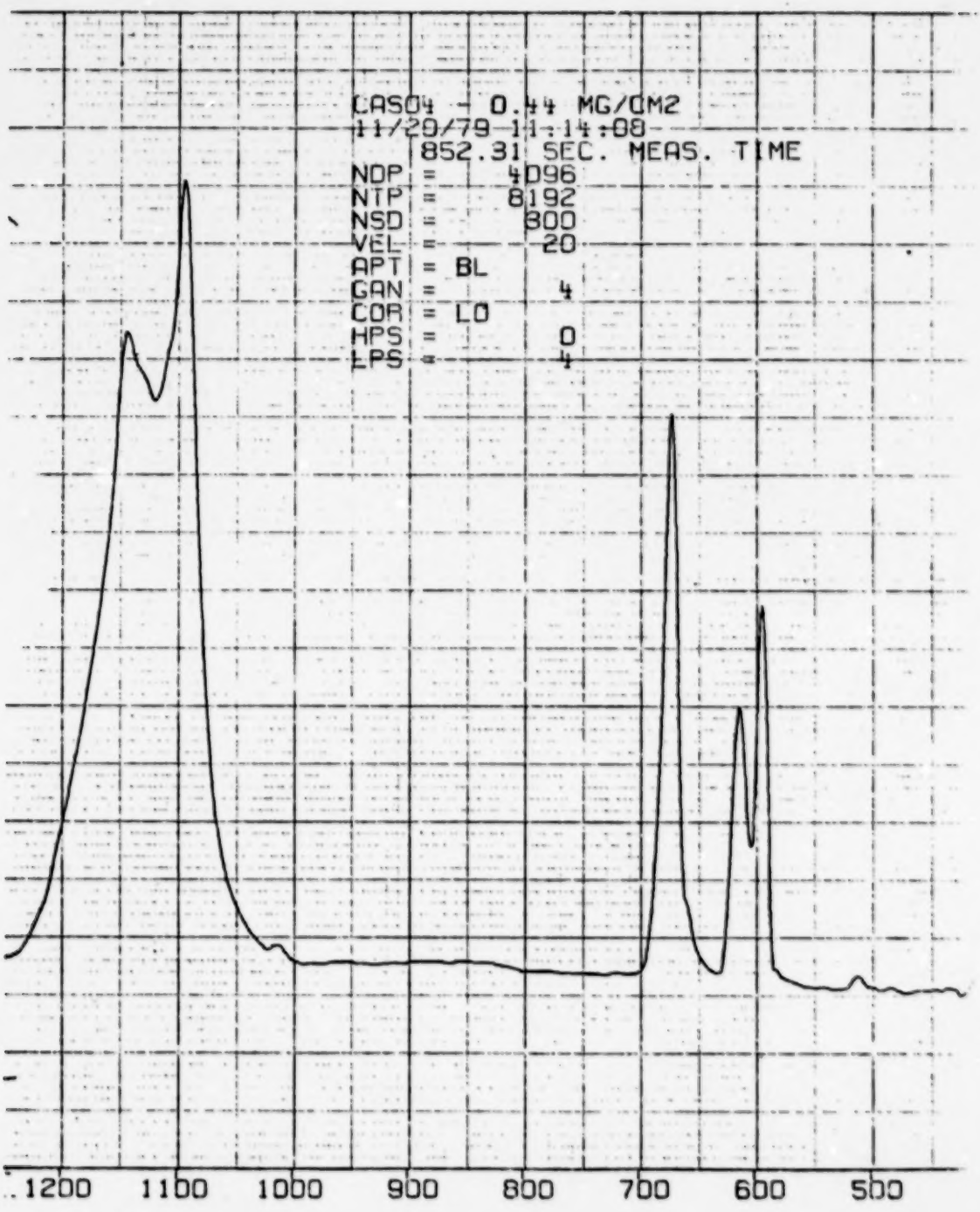

Figure D-6. Calcium Sulfate Standard

167-CC, 167-1C and 167-PF

Both the 167-1C and 167-PF samples (Figures D-7, D-8, D-9) were very similar. Very few bands were present in either sample. The predominant bands at 1070 (s,b) and 470 (m) cm^{-1} can be assigned to the silicate matrix of the fly ash. In addition, in 167-1C, there is a weak band at 795 (w) cm^{-1} which can be assigned to crystalline SiO_2. Very weak evidence for the presence of Fe_3O_4 is found in the weak broad band at 570 cm^{-1}. There is possibly some reason to suspect a sulfate compound is present in 167-PF due to the weak band at 610 cm^{-1}, but there is not enough definition to indicate the exact compound. Finally, 167-PF shows a weak band (SiO_2) at 795 cm^{-1}.

The 167-CC sample has the same bands as 167-PF/1C, and several others. SiO_2 is present at levels higher than in either 167-1C or 167-PF. Weak evidence for Fe_3O_4 is found in the 570 (w) cm^{-1}. The sharp bands to either side of 460 cm^{-1} are unknown, but appear to be related to a water soluble heat labile compound. The main band in the spectrum at 1070 cm^{-1} shows some unsymetrical character in the 1100 cm^{-1} region, indicating the presence of another compound. Sulfate bands occur in that region, but only very weak bands at 610, 600, and 590 cm^{-1} were found. These bands are in the $CaSO_4$/ $NaHSO_4$ region. Because of their low intensity, no definite assignment can be made.

168-CC and 168-FC

Both 168-CC and 168-FC (Figures D-10 and D-11) have very few discernible bands. The typical silicate matrix bands at 1070 (s,b) and 470 (m) are present. There appears to be some SiO_2 in 168-CC but little or none in 168-FC. There is some evidence of a sulfate being present in 168-FC at 605 cm^{-1} (w,b), but no definitive compound could be assigned.

169-CC and 169-FC

In contrast to the 168 samples, the 169-CC and 169-FC spectra (Figures D-12 and D-13) have much more detail. Both SiO_2 and silicate bands are present in 169-CC. In addition, there is a band at 610 cm^{-1} which is in the sulfate region. There is a shoulder at 1120 cm^{-1} which also indicates a sulfate compound. The elemental data show that Fe, Al, Na, and Ca are present in the highest quantities in 169-CC. Both Fe and Al are expected

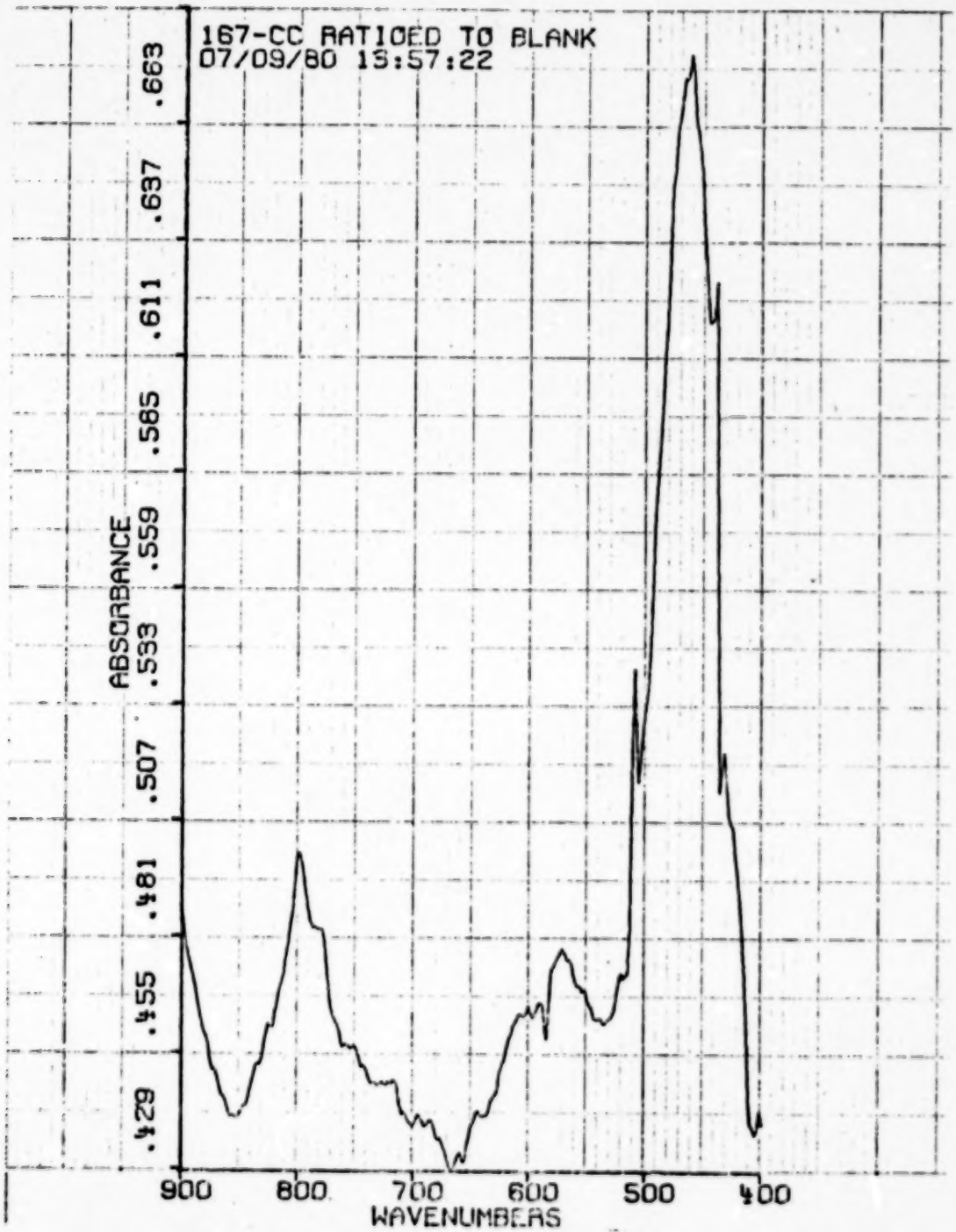

Figure D-7. ESP Inlet Particulate Larger than 3 μm

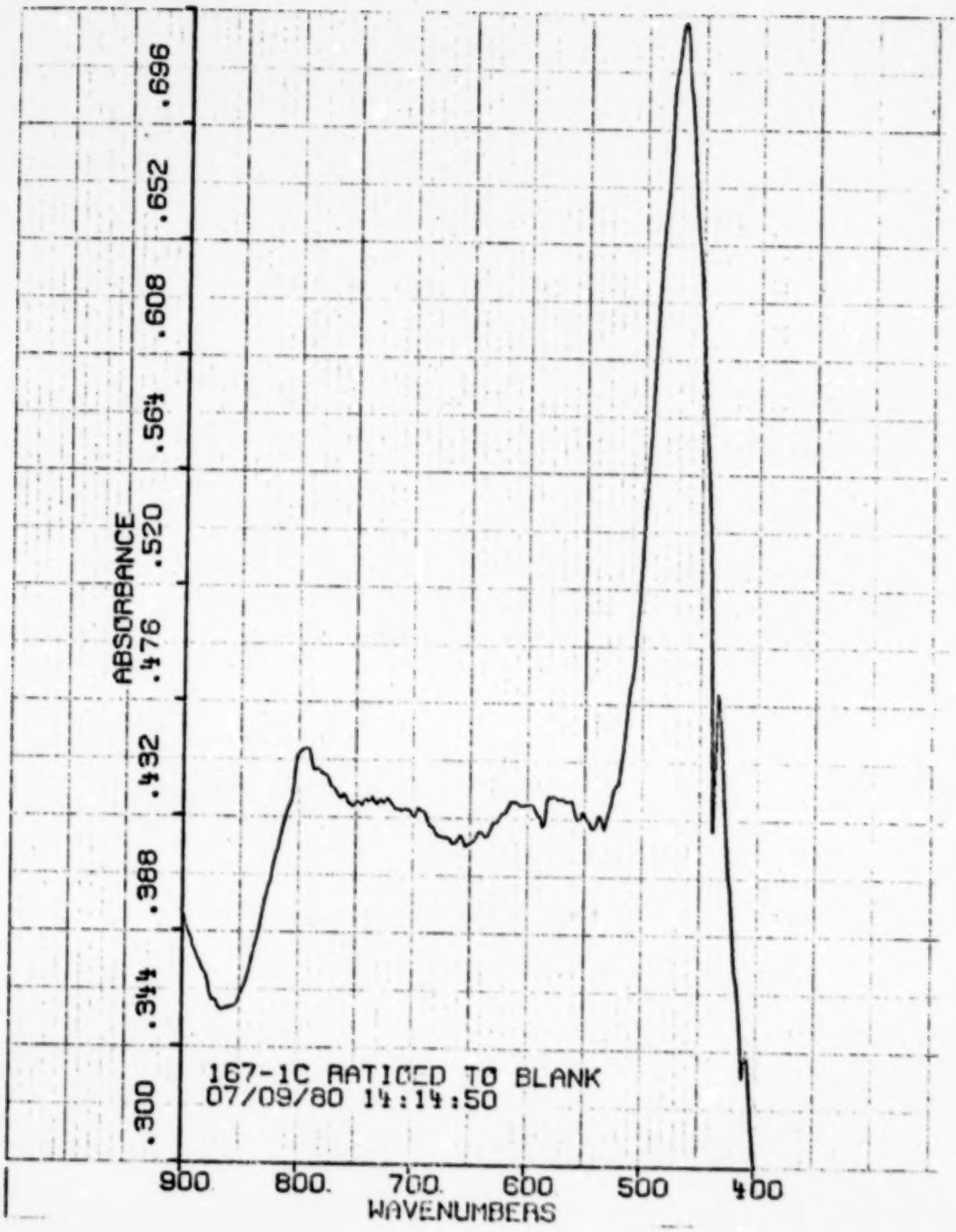

Figure D-8. ESP Inlet Particulate, 1-3 μm

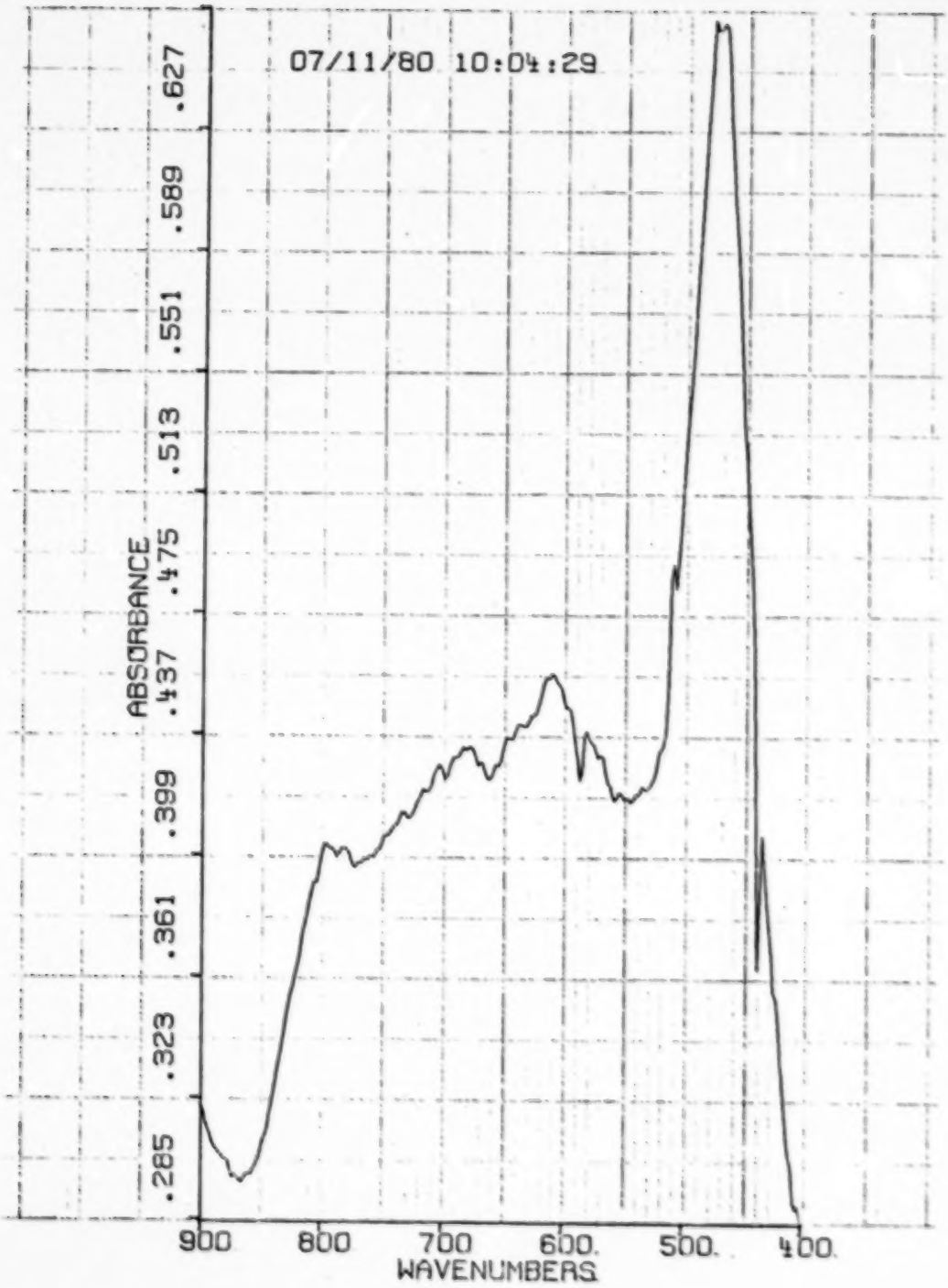

Figure D-9. HCl Extracted ESP Inlet Particulate Larger than 3 μm

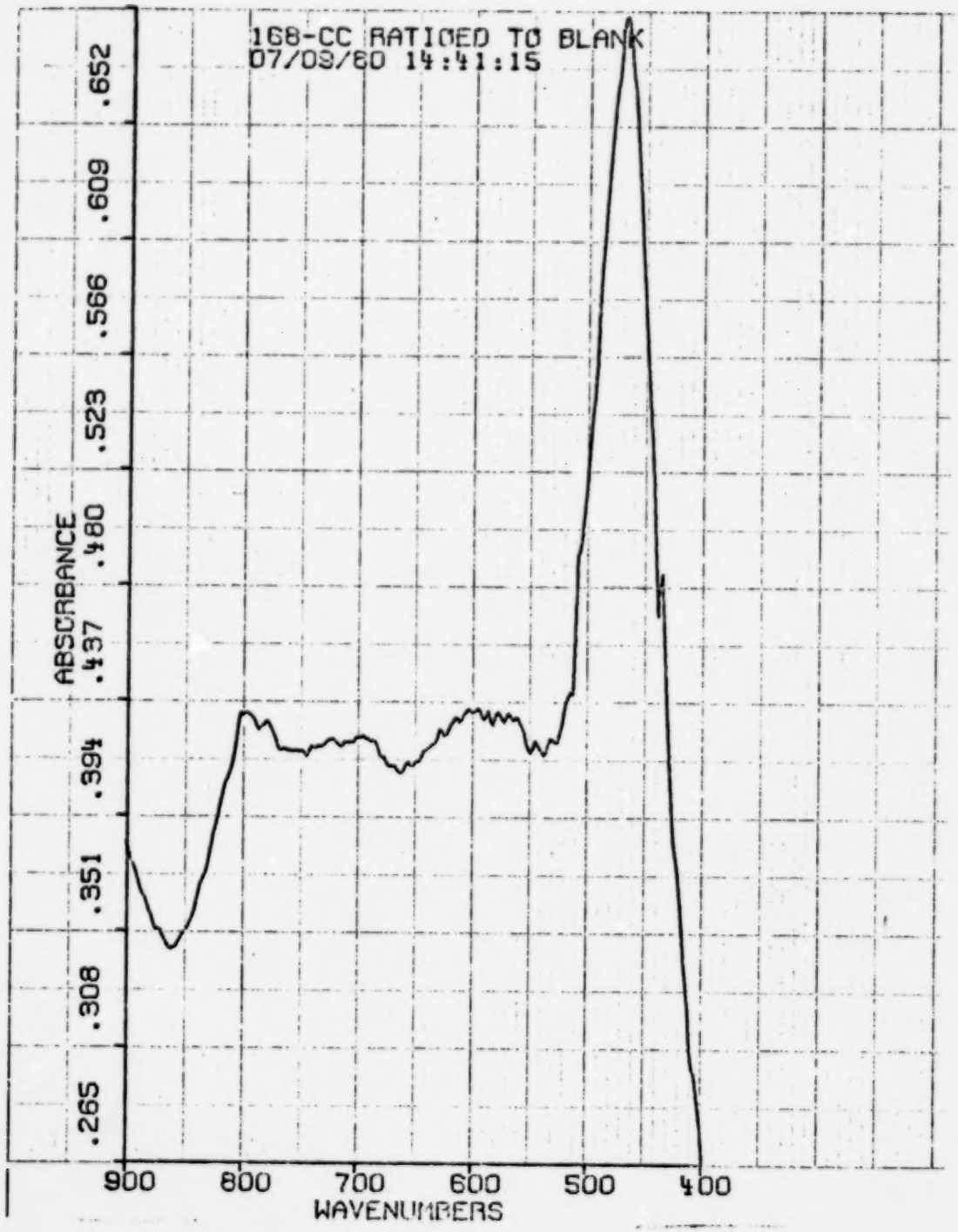

Figure D-10. ESP Outlet Particulate Larger than 3 μm

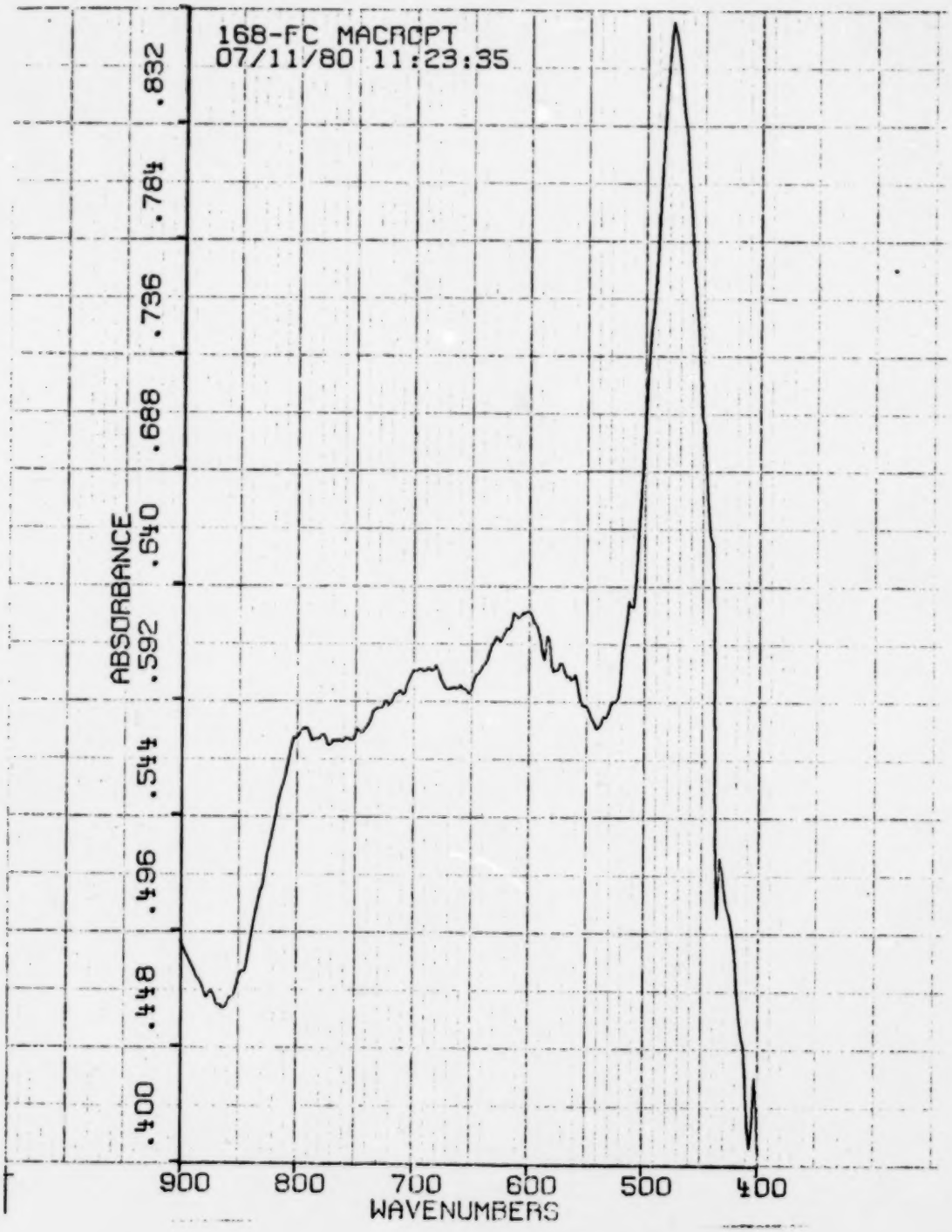

Figure D-11. ESP Outlet Particulate Smaller than 3 μm

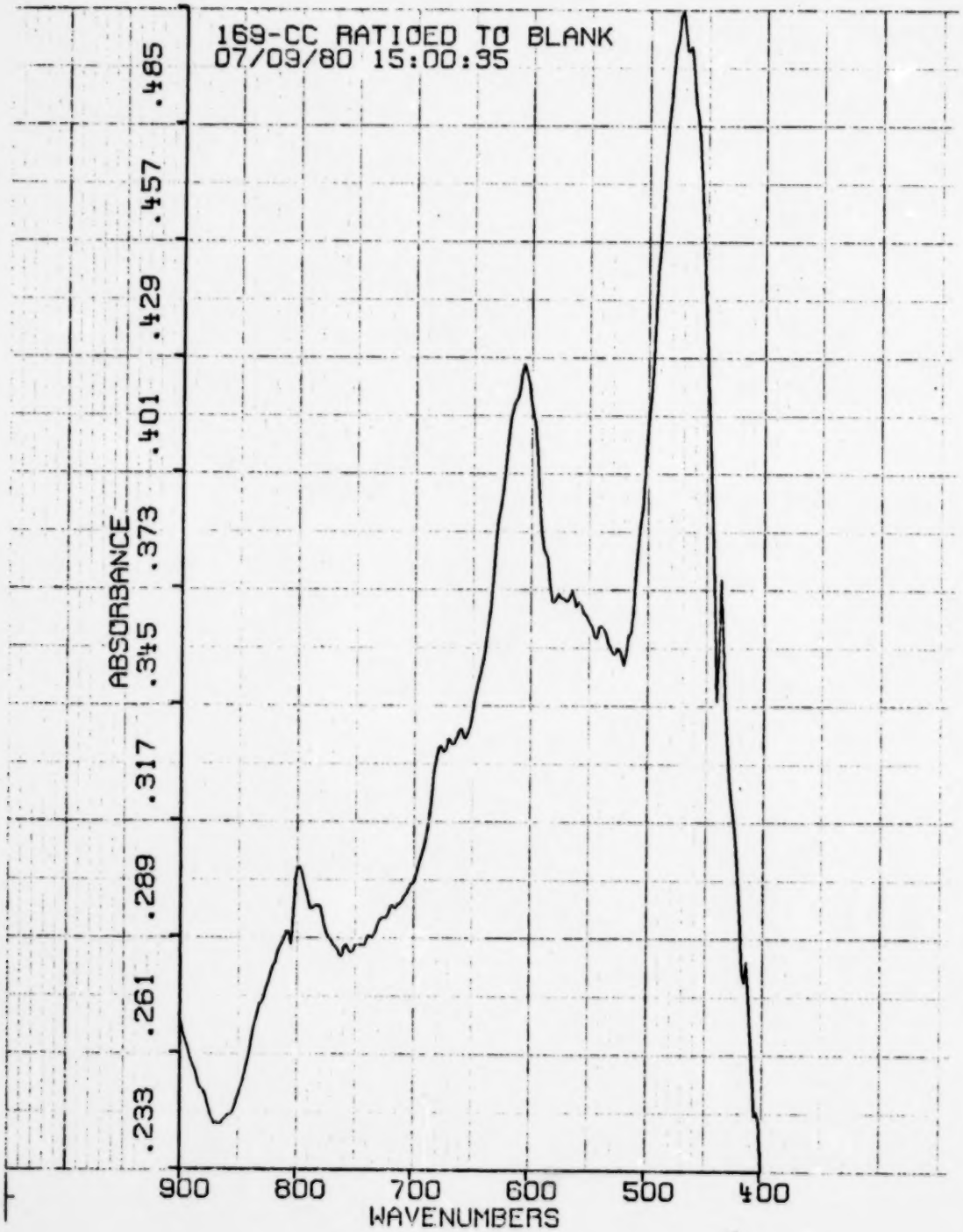

Figure D-12. Scrubber Outlet Particulate Larger than 3 μm

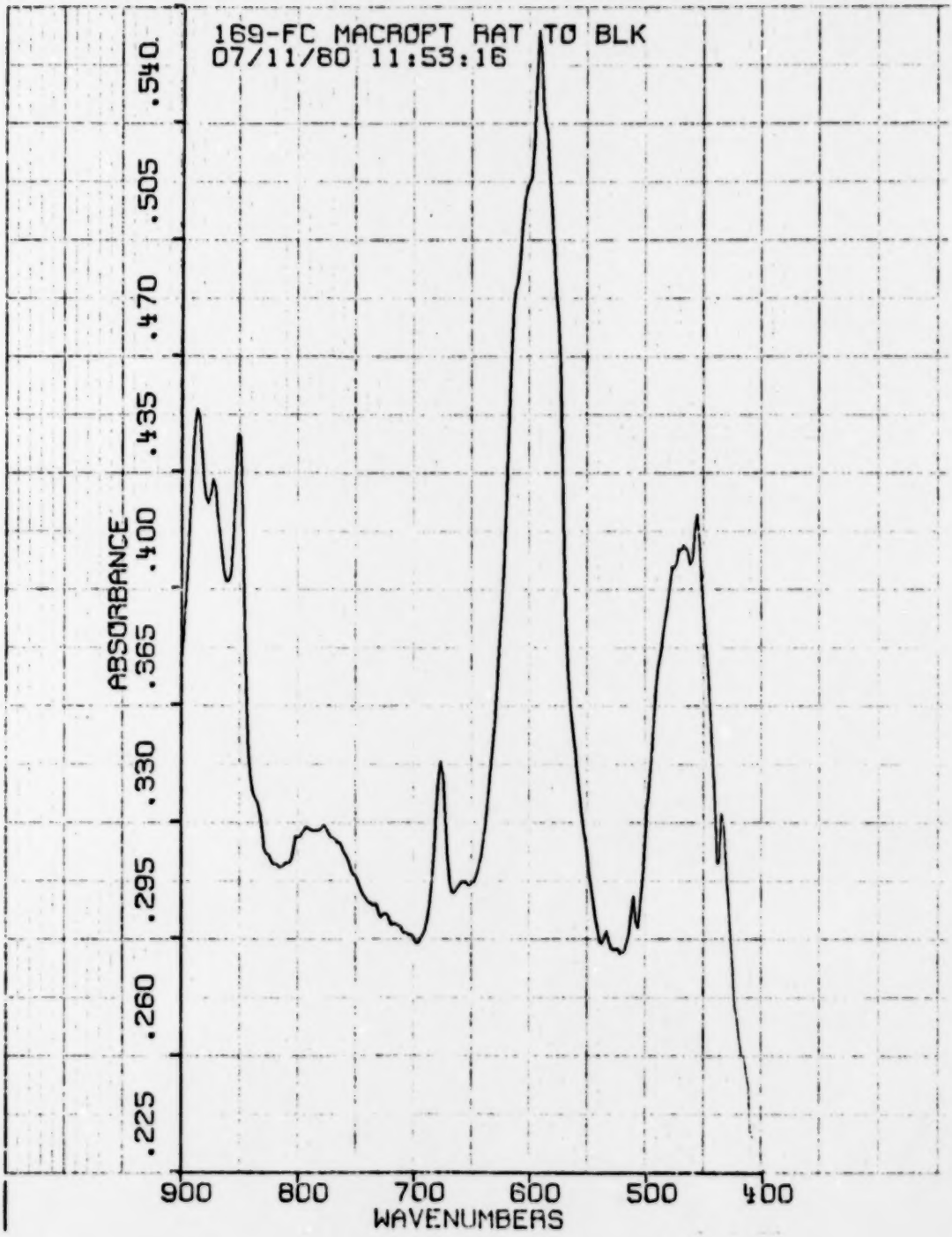

Figure D-13. Scrubber Outlet Particulate Smaller than 3 μm

to be part of the fly ash matrix. Sulfates (or bisulfates) of Na and Ca all have additional bands in 600, 700, or 800 cm^{-1} regions. Both NH_4HSO_4 and $(NH_4)_2SO_4$ also have bands in the 700 cm^{-1} region. These compounds must be considered since H_2SO_4 collected on the filter can scavenge NH_3 from the air during sample storage. The only compound which might fit is NH_4NaSO_4 which has a band at 620 cm^{-1} but no others in the 400 to 900 cm^{-1} region. It is suspected that $NaHSO_4$ on the filter scavenged NH_3. The $NaHSO_4$ could have come from:

1. the H_2SO_4 collected on the fly ash particles, which then leached Na^+ from the fly ash;
2. $NaHSO_3$ emitted by the scrubber and then oxidized to $NaHSO_4$.

Particulate matter from 169-FC had a very interesting spectrum. No SiO_2 was found, but the silicate fly ash matrix was still present, though at a decreased level, compared to all the other samples. Bands at 885, 870, 800, and 405 cm^{-1} are due to NH_4HSO_4 (see Figure D-14). Shoulders at 1170, 585, and 620 cm^{-1} are also due to $NaHSO_4$. The reasons for the appearance of $NaHSO_4$ are the same, except that the glass fiber filter itself could be a source of leachable sodium. In addition to the $NaHSO_4$, the presence of $CaSO_4 \cdot 2H_2O$ is indicated by the 675 cm^{-1} band and the 590 cm^{-1} band. The band at 590 cm^{-1} is distorted due to the overlap from the $NaHSO_4$ bands. Bands at 1150 and 1100 cm^{-1} confirm the presence of $CaSO_4 \cdot 2H_2O$.

Discussion

Table D-2 summarizes the results of this FTIR study. It compares the compounds found to the next larger particle size sample, and samples of equivalent particle size across the control device. Clearly the particulate matter composition of the <3 μm particles emitted from the scrubber are different than the inlet. $CaSO_4$ and $NaHSO_4$ are present. The concentration of the silicate matrix also appears to have decreased. The $NaHSO_4$ could be a partial neutralization product from the action of H_2SO_4 leaching Na from the fly ash or glass fiber filter, or it could be from the oxidation of $NaHSO_3$ from entrained scrubber liquor. The latter explanation would explain the appearance of $CaSO_4$, since the scrubber liquor stream in the FGD also contains Ca^{+2} and $SO_4^=$ ions. Evaporation of the scrubber liquor (or

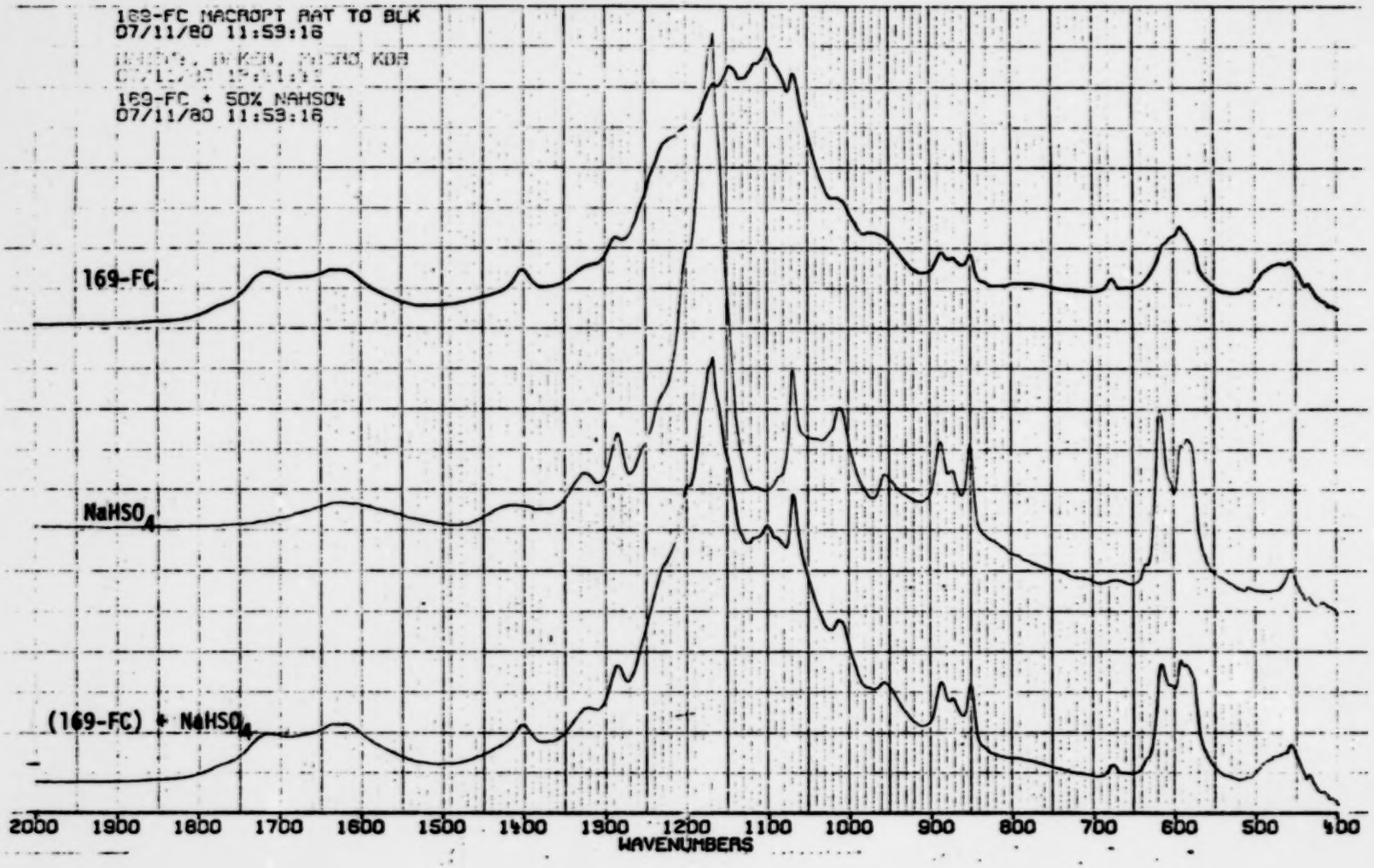

Figure D-14. Scrubber Outlet Particulate Less than 3 μm Expanded Spectrum showing $NaHSO_4$ standard and addition spectra.

TABLE D-2. SUMMARY OF FTIR ANALYSIS OF CANE RUN FLUE GAS PARTICULATE MATTER

Sample	Sample Type and Location	Species Found	Certainty of Identification	Concentration Comparison Between Particle Sizes	Concentration Comparison Between Locations
167-CC	10 + 3 μm cyclone catch at the ESP inlet	SiO_2 "Silicate matrix" Fe_3O_4	Strong Strong Very weak	Not Applicable	Not Applicable
167-1C	1 μm cyclone catch at the ESP inlet	"Silicate matrix" Fe_3O_4 SiO_2	Strong Weak Weak	Same as 167-CC Less than 167-CC Less than 167-CC	Not Applicable
167-PF	Filter catch at ESP inlet	"Silicate matrix" SiO_2 $CaSO_4$	Strong Weak Weak	Same as 167-1C Much less than 167-1C Not Applicable	Not Applicable
168-CC	10 and 3 μm cyclone catch at the scrubber inlet	SiO_2 "Silicate matrix"	Moderate Strong	Not Applicable	Less than 167-CC Same as 167-CC
168-FC	Filter and 1 μm cyclone catch at the scrubber inlet	"Silicate matrix" SiO_2 (Unknown sulfate)	Strong Weak Not Applicable	Same as 168-CC Less than 168-CC Not Applicable	More than 167-FC Much less than 167-FC Not Applicable
169-CC	10 and 3 μm cyclone catch at the scrubber outlet	$NaHSO_4$ "Silicate matrix" SiO_2	Strong Strong Moderate	Not Applicable	Not Applicable Same as 168-CC More than 168-CC
169-PF	Filter catch at the scrubber outlet	$CaSO_4$ $NaHSO_4$ "Silicate matrix"	Strong Strong Strong	Not Applicable More than 169-CC Less than 169-CC	Not Applicable Not Applicable Less than 168-FC

mist eliminator spray water) would leave solid aerosols reflecting the composition of the dissolved solids. Table D-3 shows that the Na concentration increased across the scrubber while the Ca concentration increased in the >3 μm size fraction and decreased in the <3 μm size fraction. The appearance of $CaSO_4$, the decrease in silicate matrix bands, and the increase in Na concentration indicate that the FGD is emitting particulate.

The maximum amount of particulate matter emitted by the scrubber can be estimated by assuming all of the excess Na is emitted as a bisulfite. Excess Na is that amount of Na emitted above the overall particulate removal rate. The total particulate removal rate was 19% across the FGD. This implies that [(224) - (134)(0.81)] 116 pg/J of Na was emitted by the FGD. Assuming the compound emitted was originally $NaHSO_3$, the actual amount of emission was 523 pg/J. This means that approximately 7% of the total particulate emitted was due to the FGD system, and equates to an equivalent of 0.48 ng/J of particulate sulfate.

TABLE D-3. CONCENTRATION OF Na AND Ca IN THE FLUE GAS STREAM BY PARTICLE SIZE (pg/J)

Element	Scrubber Inlet			Scrubber Outlet		
	168-CC	168-FC	Total	169-CC	169-FC	Total
Na	9.8	124	134	67	157	224
Ca	23	143	166	41	83	124